Adsorption and inhibition performance of the novel cationic Gemini surfactant as a safe corrosion inhibitor for carbon steel in hydrochloric acid

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ABSTRACT
The new synthesized cationic Gemini surfactant (CGS) was tested as a corrosion inhibitor for carbon steel (CS) in 1.0 M hydrochloric acid using weight loss, electrochemical spectroscopy and potentiodynamic polarization. The inhibition efficiency is increased by increasing the CGS concentration and is almost constant within the temperature range studied. The inhibition was explained by adsorption of the CGS molecule on the CS surface. A mixed-type inhibitor is suggested for the inhibitory effects of CGS as revealed by the potentiodynamic polarization technique. The changes in impedance parameters suggested that the adsorption of the inhibitor on the CGS surface led to the formation of protective films. The adsorption of the CGS on the surface of CS obeys Langmuir adsorption isotherm. Thermodynamic and kinetic parameters were calculated and discussed.

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Steel; EIS; weight loss; polarization; acid inhibition; interfaces

1. Introduction
There are different ways to protect metals and alloys from damage caused by corrosion. One of these methods is applied on the inhibitor to retard the dissolution of CS in acid solutions. The use of organic compounds as additives to acid corrosion is a subject of continual interest to researchers because of many industrial applications, such as acid pickling, sediment removal and oil well cleaning (1). Thus, many organic compounds containing nitrogen, oxygen, sulfur and/or phosphorus were studied by many researchers (2–8). They act by adsorption on the steel surface that occurs through heterogeneous atoms, π bonds or aromatic rings. The inhibition efficiency follows the sequence O < N < S < P (9). The interactions between the organic molecule and the solid surface are primarily physical and/or chemical adsorption. The choice of suitable inhibitors depends mainly on the type, concentration and temperature of the acid.

The acidization of an oil well is an important stimulation technique for enhancing oil production. It is brought about by using a kind of solution of concentrated hydrochloric acid. To reduce aggressive acid attacks on tubing and casing materials, inhibitors were incorporated into the acid solution during the acidizing process (10). Several previous studies have shown that acidic inhibitors are effective during acidification under high temperature (11–13). To date, many authors have used surfactant as effective inhibitors for corrosion of iron or steel in acidic media (14–25).

The aim of this research is to report the inhibition performance of the CGS toward the corrosion of CS in 1 M HCl by weight loss, potentiodynamic polarization and...
electrochemical impedance techniques. The effect of temperature was studied and some thermodynamic functions were computed and explained.

2. Materials and experimental techniques

2.1. Synthesis of inhibitor

In this study, the inhibitor was synthesized through three steps. In the first step, the quaternization reaction of 1-bromododecane with an appropriate amount of 2-(dimethyl amino) ethanol in the molar ratio of 1:1 was carried out to produce N-(2-hydroxyethyl)-N,N-dimethyl-dodecan-1-aminium bromide (I2). The reagents were allowed to reflux in ethanol for 12 h. Then, the reaction mixture was left to cool at room temperature. The precipitate was further purified by diethyl ether, then crystallized from ethanol. In the second step, the esterification reaction of the synthesized quaternary ammonium salt and citric acid in the presence of toluene as a solvent and p-toluene sulfonic acid as a dehydrating agent (14) in the molar ratio of 1:2 was carried out to produce N,N'-(4-carboxy-3-hydroxybutanoyl) bis (Oxy)) bis (ethane-2,1-diyl)) bi's (N,N-dimethyl-dodecan-1-aminium) bromide. The reaction was completed when the water was removed from the reaction system. The reaction mixture was distilled under vacuum to completely remove the solvent. In the third step, the product of the second step and polyethylene glycol were esterified as described in the second step in the molar ratio of 1:2 to N-dodecyl-6-(2-(dodecyl(dimethylammonio) ethoxy)-6,35-dihydroxy-N,N-dimethyl-4,8-dioxo-2,9,12,15,18,21,24,27,30,33-decaoxapentatriacontan-1-aminium) bromide.

The chemical structure of the synthesized inhibitor (Figure 1) was described by FTIR and 1HNMR, spectroscopic analyses.

2.2. Carbon steel (CS)

The chemical composition of the CS sample used in this study is (wt.%): 0.19% C, 0.05% Si, 0.94% Mn, 0.009% P, 0.004% S, 0.014% Ni, 0.009% Cr, 0.034% Al, 0.016% V, 0.003% Ti, 0.022% Cu, and balance Fe.

2.3. Weight loss measurements

The CS specimens with a dimension of 5 cm × 3 cm × 0.5 cm were abraded with a series of emery paper (grade 320–500–800–1000–1200) and washed with distilled water and acetone. After weighing accuracy, the samples were immersed in a closed beaker containing 100 ml of 1.0 M HCl solution with and without different concentrations of the synthesized inhibitor at various temperatures in the range 20–80°C. The temperature was adjusted by water bath supplied with a thermostat control ±1°C. The CS specimens were taken out after 24 h. Then rinsed with distilled water two times and degreased with acetone. Afterward, the specimens were immersed in 1 M HCl solution for 10 s (chemical method for cleaning rust products), rinsed twice with distilled water, dried, and accurately weighted. Each experiment was repeated three times and the average value was taken. Then, the tests were repeated at different temperatures.

2.4. Electrochemical measurements

Potentiodynamic polarization experiments were performed using a conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as a reference electrode. The working electrode (WE) was a CS rod embedded in the PVC holder using epoxy resin so that the flat surface was the exposed area of the electrode. Before each measurement, the electrode was immersed in a test solution at an open circuit potential (OCP) for 30 min, until a steady state was reached. The choice of this time is due to the following: when the CS electrode is immersed in the test solution, the OCP is changed rapidly and then after a certain time the value of OCP is constant. This potential is known as the steady-state potential or corrosion potential.

![Figure 1. Chemical structure of the synthesized novel cationic Gemini surfactant (CGS).](image-url)
All polarization curves were recorded by a Voltalab 40 Potentiostat PGZ 301 and a personal computer was used with Voltamaster 4 software at 20°C. Potentiodynamic polarization (PP) measurements were obtained by automatically changing the electrode potential from −800 to −300 mV vs. SCE at open circuit potential with a scan rate of 2 mV s\(^{-1}\) at 20°C. Electrochemical impedance spectroscopy (EIS) measurements were performed as described previously (15). A small alternating voltage perturbation (5 mV) was imposed on the cell over the frequency range of 100 kHz–30 mHz at 20°C.

3. Results and discussions

3.1. Chemical structure confirmation of the synthesized surfactants

3.1.1. FTIR spectra

FTIR spectra showed that the characteristic bands for the alkyl part were at 2948.86 and 2890.81 cm\(^{-1}\) for asymmetric and symmetric stretching (CH), respectively. But, they were observed at 1334.81 cm\(^{-1}\) for symmetric bending (CH\(_3\)), at 1438.77 cm\(^{-1}\) for symmetric bending (CH\(_2\)), and at 725.61 cm\(^{-1}\) for –(CH\(_2\))\(_n\)– rock. C–O stretching band 1240.39.12 cm\(^{-1}\), C–N\(^+\) at 1034.04 cm\(^{-1}\), C=O at 1768.08 cm\(^{-1}\), 3437.86 cm\(^{-1}\) was due to stretching OH. FTIR spectra confirmed the expected functional groups in the synthesized CGS compound, as shown in Figure 2.

3.1.2. \(^1\)HNMR spectra

The \(^1\)H NMR spectra of the synthesized CGS compound showed different bands at \(\delta = 0.8004–0.8272\) ppm (t, 6H, NCH\(_2\)CH\(_2\)(CH\(_2\))\(_n\)CH\(_3\)); \(\delta = 1.2037\) ppm (m, 36H, NCH\(_2\)
CH\(_2\)(CH\(_2\))\(_n\)CH\(_3\)); \(\delta = 1.6023\) ppm (m, 4H, NCH\(_2\)CH\(_2\)(CH\(_2\))\(_n\)CH\(_3\)); \(\delta = 2.4672–2.9853\) ppm (m, 4H, NCH\(_2\)OCH\(_2\)COCH\(_2\)O); \(\delta = 3.30120–3.3569\) ppm (m, 32H, CH\(_3\)N, NCH\(_2\)CH\(_2\)CCO (CH\(_2\)CH\(_2\)O)\(_n\)CH\(_2\)CH\(_2\)OH); \(\delta = 3.9773–4.111\) ppm (t, 6 H, COO CH\(_2\)CH\(_2\)O(CH\(_2\)CH\(_2\)O)\(_n\)CH\(_2\)CH\(_2\)OH); \(\delta = 4.5795\) (s, 4 H, COCH\(_3\)); \(\delta = 5.6939–5.7512\) (s, 2 H, NCH\(_2\)OCH\(_2\)), as shown in Figure 3.

![Figure 2. FTIR spectrum of the novel cationic Gemini surfactant (CGS).](image-url)

![Figure 3. \(^1\)HNMR spectrum of the novel cationic Gemini surfactant (CGS).](image-url)
3.2. EIS measurements

The Bode curves (Figure 4) show only one maximum peak at the phase angle versus the frequency plot. This maximum phase angle can be connected to the double-layer capacitance. The high frequency loop returns to the capacity of the double layer and is parallel to the charge transfer resistance. Figure 5 shows the typical Nyquist diagram of CS in HCl 1 M solution with and without different concentrations of CGS. It is clear that the addition of CGS leads to an increase in the diameter of the semicircle capacitive loop and at the maximum phase angle. Inspections of the data reveal that the Nyquist plot obtained for inhibitor appears to exhibit a depressed loop; such behaviors are mostly referred to as frequency dispersion, indicating irregularities and heterogeneity of solid surfaces (26).

In particular, the high-frequency part of the impedance and phase angle reflects the behavior of heterogeneous surface layer, while the low-frequency part shows the kinetic response to the charge-transfer reaction.
interaction (27). In order to obtain more accurate results, the analysis of the complex plane diagram was performed by constructing experimental results in the equivalent circuit shown in Figure 6, previously used for the CS–acid interface model (13). The use of a fixed phase element (CPE) can be an effective way of representing the frequency dependence of non-ideal capacitive behavior. The impedance of the CPE is given by (28)

\[ Z_{\text{CPE}} = Q - 1 (i \omega_{\text{max}})^n - 1 \]

where \( Q \) is the constant phase element, \( \omega_{\text{max}} \) is the angular frequency in rad S\(^{-1}\), \( \omega = 2nf_{\text{max}} \) (where \( f \) is the frequency at which the imaginary component of the impedance is maximum), \( i \) is the imaginary number and \( n \) is a coefficient that can be used as a measure of surface inhomogeneity. Depending on the value of \( n \), CPE can represent resistance \((n = 0, Q = 1/R)\), capacitance \((n = 1, Q = C)\), inductance \((n = -1, Q = 1/L)\) or Warburg impedance \((n = 0.5, Q = W)\). The values of \( n \) were in the range from 0.7 to 0.95, indicating non-ideal capacitive behavior.

The circuit consists of solution resistance \( (R_s) \) in series with a parallel combination of charge-transfer resistance \( (R_{\text{ct}}) \) and a constant phase element, CPE used in place of the double-layer capacitance \( (C_{\text{dl}}) \) to represent the non-ideal capacitive behavior of the double layer more clearly. The values of inhibition efficiency \((\eta)\) of the charge-transfer resistance were calculated from the following equation:

\[ \eta = \frac{R_{\text{ct}} - R_{\text{ct}}^\text{inh}}{R_{\text{ct}}} \times 100 \]

where \( R_{\text{ct}} \) and \( R_{\text{ct}}^\text{inh} \) are the charge-transfer resistance values with and without inhibitor, respectively. The results obtained from this complex plot are presented in Table 1. The \( C_{\text{dl}} \) values were calculated using the following equation (29):

\[ C_{\text{dl}} = Q(\omega_{\text{max}})^n - 1 \]

From Table 1, it is clear that the \( R_{\text{ct}} \) value of CS in uninhibited solution increases significantly after the addition of the CGS. Also, the addition of the CGS to a corrosive solution reduces the double-layer capacitance. The double layer between the surface of the charged metal and the solution as an electrical capacitor. The reduction of this capacitance can be attributed to the gradual replacement of water molecules by the adsorption of the CGS at the CS–solution interface. The adsorption process followed by the formation of a surface layer film of the inhibitor protects the metal against corrosion (26). EIS revealed that the corrosion inhibition efficiency of the CGS increases with increasing CGS concentration.

### 3.3. PP measurements

Figure 7 shows PP curves for CS in 1 M HCl in the absence and presence of various concentrations of the CGS. Table 2 shows the values of associated corrosion parameters such as corrosion potential \((E_{\text{corr}})\), anodic Tafel slopes \((\beta_a)\), cathodic Tafel slopes \((\beta_c)\), and corrosion current density \((i_{\text{corr}})\). The inhibition efficiency \(\eta_p\) (%) was calculated from PP measurements according to the following relationship (12):

\[ \eta_p = \frac{i_{\text{corr}} - i_{\text{corr}}^\text{inh}}{i_{\text{corr}}} \times 100 \]

where \( i_{\text{corr}} \) and \( i_{\text{corr}}^\text{inh} \) are the corrosion current densities for CS electrode in the uninhibited and inhibited solutions, respectively.

Table 2 shows that the values of anodic and cathodic Tafel constants \( \beta_a \) and \( \beta_c \) have changed slightly so that the CGS is a mixed type because it reduces the anodic dissolution of CS and retards the cathodic hydrogen evolution reaction. The presence of CGS does not significantly shift the corrosion potential \((E_{\text{corr}})\). This indicates that the corrosion mechanism of CS in 1 M HCl solution does not change after adding the inhibitor. This inhibitor is first adsorbed on the CS surface, thus reducing the available surface area for corrosion reactions simply by preventing the interaction sites of the CS surface (30, 31). The values of \( i_{\text{corr}} \) are reduced with increased CGS concentration, suggesting that the presence of this CGS retards the dissolution of CS in 1 M HCl solution and the degree of inhibition depends on the concentration.

![Figure 6](image-url) **Figure 6.** The electrical equivalent circuit used for modeling the interface steel/1.0 M HCl solution in the absence and presence of the CGS molecule.

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**Table 1.** EIS parameters for corrosion of CS in 1 M HCl in the absence and presence of different concentrations of the synthesized novel CGS at 20°C.

| Conc. of inhibitor (M) | \( R_s \) (Ω cm\(^2\)) | \( R_{\text{ct}} \) (Ω cm\(^2\)) | \( C_{\text{dl}} \) (μF cm\(^{-2}\)) | \( \eta \) (%) |
|-----------------------|--------------------------|--------------------------|----------------------------|-------------|
| 0.00                  | 2.1                      | 43.6                     | 102.2                      | –           |
| 5 × 10\(^{-5}\)       | 286.5                    | 27.77                    | 85.17                      |
| 1 × 10\(^{-4}\)       | 3308                     | 67.35                    | 98.72                      |
| 5 × 10\(^{-4}\)       | 453.6                    | 17.54                    | 90.63                      |
| 1 × 10\(^{-3}\)       | 546.5                    | 23.29                    | 92.23                      |
| 5 × 10\(^{-3}\)       | 747.6                    | 21.28                    | 94.32                      |
3.4. Weight loss measurement

The corrosion rate \( k \) and inhibition efficiency \( \eta_w \) were calculated using the following equations \((14,26)\):

\[
k = \frac{\Delta W}{A \Delta t} \tag{5}
\]

\[
\eta_w = \frac{(k_{\text{free}} - k_{\text{inh}})}{k_{\text{free}}} \times 100 \tag{6}
\]

where \( \Delta W \) the average weight loss, \( k_{\text{free}} \) and \( k_{\text{inh}} \) the corrosion rates of weight loss of CS in 1 M HCl in the absence and presence of different concentration of the CGS, respectively, \( A \) is the surface area in cm\(^2\) and \( t \) is the time in hours. Table 3 presents data obtained from weight loss measurements. It was observed that the weight loss was significantly reduced in the presence of the CGS compared to the blank acid solution and found to be dependent on the inhibitor concentration. This suggests that CGS additives retard CS corrosion in 1 M HCl solution, suggesting an increase in inhibition efficiency by increasing concentration.

3.5. Effect of temperature

Like most chemical reactions, the corrosion rate of CS increases with temperature, especially in acid media due to hydrogen evolution. Acid pickling of CS is usually done at elevated temperatures up to 60°C in HCl. Accordingly, pickling inhibitors are expected to be chemically stable to provide high protective efficiency under the above conditions \((32)\). An inspection of the values given in Table 3, the inhibition efficiency of CGS is almost constant at the studied temperature range.
The corrosion rate of CS increases rapidly with temperature in the absence of inhibitor. This finding confirms that the inhibitor acts as an effective inhibitor within the temperature range studied.

### 3.6. Adsorption isotherm

The adsorption of CGS on the surface of CS can be considered as a substitution process between CGS in the aqueous phase (CGS\textsubscript{soln}) and water molecules adsorbed on the surface of the CS (H\textsubscript{2}O\textsubscript{ads}) as given in the following equation (33).

\[
\text{CGS}_{\text{soln}} + x \text{H}_{\text{ads}} \leftrightarrow \text{CGS}_{\text{ads}} + x \text{H}_{\text{soln}} \quad (7)
\]

where \(x\) represents the number of water molecules that are replaced by one molecule of adsorbed CGS. The above process is balanced when the chemical potential in the left hand is equal to that on the right side.

The degree of surface coverage (\(\theta\)) was determined at a constant temperature of the following equation (13).

\[
\theta = \frac{W_{\text{free}} - W_{\text{inh}}}{W_{\text{free}}} \quad (8)
\]

where \(W_{\text{free}}\) and \(W_{\text{inh}}\) are weight losses for CS due to the dissolution in 1 M HCl in the absence and presence of different concentrations of inhibitor, respectively.

Adsorption isotherm is very important in determining the mechanism of electrochemical reactions. I have tried many attempts to find the most appropriate isotherms, for example, Langmuir, Frumkin, Temkin, Flory-Huggins, and Bockris-Swinkels (34). Langmuir is found to be a suitable isotherm. Figure 8 shows that the Langmuir adsorption isotherm for CS in 1 M HCl is drawn as \(C/\theta\) vs. \(C\). The straight line is obtained with a slope equal to approximately the unit and the intercept equal to \((1/K_{\text{ads}})\). The experimental data are suitable for the isotherm adsorption of Langmuir, as represented in the following Table 3. Corrosion rate of CS, surface coverage and percentage inhibition efficiency for CS in 1 M HCl in the absence and presence of different concentrations of novel CGS from weight loss measurements at different temperatures.

| Conc. of inhibitor (M) | 20°C | 40°C | 60°C | 80°C |
|-------------------------|------|------|------|------|
|                         | \(k\) (mg cm\(^{-2}\) h\(^{-1}\)) | \(\eta_c\) (%) | \(k\) (mg cm\(^{-2}\) h\(^{-1}\)) | \(\eta_c\) (%) | \(k\) (mg cm\(^{-2}\) h\(^{-1}\)) | \(\eta_c\) (%) | \(k\) (mg cm\(^{-2}\) h\(^{-1}\)) | \(\eta_c\) (%) |
| 0.00                    | 0.4192 | 0.00 | 0.00 | 1.6996 | 0.00 | 5.7325 | 0.00 | 16.0965 | 0.00 |
| \(5 \times 10^{-5}\)    | 0.0637 | 0.85 | 84.81 | 0.2549 | 0.85 | 85.00 | 0.8753 | 0.85 | 84.73 | 2.4145 |
| \(1 \times 10^{-4}\)    | 0.0566 | 0.87 | 86.50 | 0.2225 | 0.87 | 86.91 | 0.7567 | 0.87 | 86.80 | 2.0942 |
| \(5 \times 10^{-4}\)    | 0.0407 | 0.90 | 90.30 | 0.1614 | 0.91 | 90.50 | 0.5503 | 0.90 | 90.40 | 1.4841 |
| \(1 \times 10^{-3}\)    | 0.0344 | 0.92 | 91.80 | 0.1410 | 0.92 | 91.70 | 0.4722 | 0.92 | 91.76 | 1.2898 |
| \(5 \times 10^{-3}\)    | 0.0247 | 0.94 | 94.10 | 0.1006 | 0.94 | 94.08 | 0.3452 | 0.94 | 93.98 | 0.9315 |

Figure 8. Langmuir isotherm model for the adsorption of the CGS on the CS surface in 1.0 M HCl at different temperatures.
equation (12):
\[ \frac{C}{\theta} = \frac{1}{K_{ads}} + C \]  
(9)

Langmuir isotherm postulates monolayer adsorption, hence no interaction between the adsorbate species on the metal surface.

The surface coverage data are clearly useful for discussing the adsorption characteristics. The large the values of \( K_{ads} \) the better the adsorption efficiency, thus better the inhibition efficiency (35). The kinetic adsorption isotherm can be written in the following form (13,36):

\[ \frac{\theta}{1-\theta} = K'Cy \]  
(10)

or this equation can be written in linear form as

\[ \ln \left( \frac{\theta}{1-\theta} \right) = \ln K' + y\ln C \]  
(11)

where \( K' \) is a constant, and \( y \) is the number of inhibitory molecules occupying one active site. A plot of \( \ln(\theta/(1-\theta)) \) versus \( \ln(C) \) gives a straight line of slope \( y \) and intercept \( \ln(K') \), as shown in Figure 9.

Equilibrium constant corresponding to adsorption isotherm is given by \( K = K'^{1/y} \). The value of \( y > 1 \) means a multi-layer formation of the inhibitor on the metal surface. The value of \( y < 1 \) means that the inhibitor molecules given will occupy more than one active location.

The values of the equilibrium constants obtained from the Langmuir model were similar to those obtained from the thermodynamic model. Also, the value of \( y \) was less than the unit, indicating a monolayer formation on the metallic surface which agrees with the assumptions of the Langmuir adsorption isotherm.

The known thermodynamic adsorption parameters, the free energy of adsorption (\( \Delta G_{ads} \)), the heat of adsorption (\( \Delta H_{ads} \)) and entropy of adsorption (\( \Delta S_{ads} \)), were calculated by the mathematical method depending on different temperatures.

The equilibrium constant of the adsorption process from Langmuir (\( K_{ads} \)) is associated with the standard free energy adsorption \( \Delta G_{ads} \) by the following expression:

\[ \Delta G_{ads} = -RT\ln(55.5K_{ads}) \]  
(12)

where \( R \) is the molar gas constant, \( T \) is the absolute temperature and 55.5 is the concentration of water in solution expressed in mol dm\(^{-3}\).

For, \( \Delta G_{ads} \), which can distinguish the interaction between adsorption molecules and metal surface (37).

![Figure 9. Kinetic–thermodynamic model for the adsorption of the CGS on the CS surface in 1.0 M HCl.](image-url)
In general, $\Delta G_{\text{ads}}$ values of up to $-20$ kJ mol$^{-1}$ correspond to the electrostatic reaction between charged molecules and charged metal (physical adsorption) while the negative values greater than $-40$ kJ mol$^{-1}$ involve the sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate bond (chemisorption) (38).

In this study, it was found that the value of $D G_{\text{ads}}^\circ$ is about $-40$ kJ mol$^{-1}$, meaning that the adsorption mechanism of CGS on the CS surface is essentially a chemisorption.

The adsorption heat can be calculated according to the Van’t Hoff equation and can also be calculated from the Gibbs–Helmholtz equation, which is defined as follows (39):

$$\ln K_{\text{ads}} = -\frac{\Delta H_{\text{ads}}}{T_2}$$

which can be arranged to give the following equation:

$$\frac{\Delta G_{\text{ads}}}{T} = -\frac{\Delta H_{\text{ads}}}{T} + \text{constant}$$

The values of the entropy of adsorption $\Delta S_{\text{ads}}$ were computed using the following equation.

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T \Delta S_{\text{ads}}$$

Figure 10 shows a variation of $\Delta G_{\text{ads}}/T$ vs. $1/T$ which gives a straight line with a slope equal to $\Delta H_{\text{ads}}$. The values of the thermodynamic adsorption parameters are listed in Table 4. Table 4 shows that the positive sign of $\Delta H_{\text{ads}}$ indicates that CGS adsorption on the CS surface is an endothermic process. The value of $\Delta H_{\text{ads}}$ was observed in the measured temperature range indicating that the inhibition of CS corrosion in these solutions was due to the chemical adsorption of the CGS on the CS surface. The positive sign of $\Delta S_{\text{ads}}$ indicates that the substitution process leads to an increase in the solvent entropy and more water desorption entropy (24).

Furthermore, the fundamental characteristic of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, $R_L$ (26), which describes isotherm type and defines it by

$$R_L = 1 + K_{\text{ads}}C$$

The smaller $R_L$ indicates very favorable adsorption. If $R_L > 1$ is unfavorable, $R_L = 1$ linearly, $0 < R_L < 1$ is favorable, and if $R_L = 0$ is irreversible. Table 5 gives the estimated value of $R_L$ to inhibitors at different concentrations. The value of the $R_L$ value was found to be less than the corresponding unit that the adsorption processes were favorable.

3.7. Inhibition mechanism

The adsorption of the CGS molecule on the surface of the CS covered with primarily adsorbed bromide ions is a

![Figure 10](image-url)

*Figure 10.* Relationship between $\Delta G_{\text{ads}}/T$ and $1/T$ of CS in the absence and presence of different concentrations of the novel CGS in 1 M HCl solution.

| Temperature (°C) | $K_{\text{ads}} \times 10^{-4}$ (M$^{-1}$) | $\Delta G_{\text{ads}}^\circ$ (kJ mol$^{-1}$) | $\Delta H_{\text{ads}}^\circ$ (kJ mol$^{-1}$) | $\Delta S_{\text{ads}}^\circ$ (J mol$^{-1}$ K$^{-1}$) |
|-----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 20              | 6.11                            | $-36.63$                        | 0.90                            | 128.10                          |
| 40              | 6.25                            | $-39.19$                        | 0.90                            | 128.09                          |
| 60              | 6.39                            | $-41.75$                        | 0.90                            | 128.10                          |
| 80              | 6.50                            | $-44.31$                        | 0.90                            | 128.10                          |
two-step process that is consistent with the results mentioned in the literature (40). Interpretation of the adsorption process depends on the concentration of CGS. First, at low concentrations, the surfactant molecules are distributed on the surface of CS, and it seems that the adsorption of Gemini surfactant molecule takes place by binding of individual Gemini surfactants on charging sites on the CS surface. This adsorption is preferred by the electrostatic interaction between the two ammonium groups (N+) and bromide ions, which is first adsorbed in the CS/solution interface by the electrostatic force of attraction. When the inhibitor concentration is increased due to the strong hydrophobicity of Gemini surfactants, the adsorption is expected to resume at a lower concentration which is the lowest for the most hydrophobic surfactant, but the first step is not yet complete. The driving force of the second adsorption step arises mainly from hydrophobic interactions between surfactant ions adsorbed in the first adsorption step and newly adsorbed ones. This results in the formation of surface micelles.

4. Conclusions

(1) CGS molecule is a good corrosion inhibitor to protect CS during the acidification process.
(2) The inhibition efficiency of CGS depends on its concentration.
(3) CGS acts as a mixed-type inhibitor.
(4) The high inhibition efficiency of the CGS molecule was demonstrated by adsorption on the CS surface and formation of a protective film formation.

(5) The adsorption of the CGS molecule on the surface of CS in 1 M HCl solution follows Langmuir isotherm.
(6) The thermodynamic parameters indicate that the CGS molecule is strongly adsorbed on the CS surface.

Disclosure statement
No potential conflict of interest was reported by the authors.

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Table 5. Values of dimensionless separation factor, $R_i$ and other thermodynamic parameters of adsorption on CS surface in 1 M HCl containing different concentrations of the synthesized novel CGS.

| Temperature (°C) | Concentration of inhibitor (M) | $R_i$ | $y$ | $K_{Kinetic}$ |
|-----------------|-------------------------------|------|----|---------------|
| 20              | $5 \times 10^{-5}$            | 0.246 | 0.2308 | $3.29 \times 10^7$ |
|                 | $1 \times 10^{-4}$            | 0.1406 |          |               |
|                 | $5 \times 10^{-4}$            | 0.0317 |          |               |
|                 | $1 \times 10^{-3}$            | 0.0161 |          |               |
|                 | $5 \times 10^{-3}$            | 0.0033 |          |               |
| 40              | $5 \times 10^{-5}$            | 0.2235 | $4.73 \times 10^7$ |               |
|                 | $1 \times 10^{-4}$            | 0.1380 |          |               |
|                 | $5 \times 10^{-4}$            | 0.0310 |          |               |
|                 | $1 \times 10^{-3}$            | 0.0158 |          |               |
|                 | $5 \times 10^{-3}$            | 0.0032 |          |               |
| 60              | $5 \times 10^{-5}$            | 0.2248 | $4.26 \times 10^7$ |               |
|                 | $1 \times 10^{-4}$            | 0.1353 |          |               |
|                 | $5 \times 10^{-4}$            | 0.0303 |          |               |
|                 | $1 \times 10^{-3}$            | 0.0154 |          |               |
|                 | $5 \times 10^{-3}$            | 0.0031 |          |               |
| 80              | $5 \times 10^{-5}$            | 0.2352 | $3.90 \times 10^7$ |               |
|                 | $1 \times 10^{-4}$            | 0.1333 |          |               |
|                 | $5 \times 10^{-4}$            | 0.0298 |          |               |
|                 | $1 \times 10^{-3}$            | 0.0151 |          |               |
|                 | $5 \times 10^{-3}$            | 0.0031 |          |               |
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