



## Effect of anion on the corrosion inhibition of cationic surfactants and a mechanism study

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### ABSTRACT

Four quaternary ammonium cationic surfactants, cetyl-trimethyl ammonium fluorine (CTAF), cetyl-trimethyl ammonium chlorine (CTAC), cetyl-trimethyl ammonium bromine (CTAB) and cetyl-trimethyl ammonium iodine (CTAI) were purchased as carbon steel corrosion inhibitors in HCl solution using weight-loss method. The correlation between inhibition efficiency and molecular structure of four inhibitors was studied. The experimental outcome showed that at the same concentration, solution temperature and HCl concentration, the inhibition efficiency of four inhibitors followed the order CTAI > CTAB > CTAC > CTAF, it seems to indicate that the type of halide ions of inhibitors greatly influence the inhibition efficiency. Based on weight loss results, the adsorption of studied inhibitors on the carbon steel surface in the HCl solution obeyed the Langmuir adsorption isotherm. The thermodynamic parameters including the standard adsorption free energy ( $\Delta G_{\text{ads}}^{\circ}$ ), the standard heat of adsorption ( $\Delta H_{\text{ads}}^{\circ}$ ) and the standard adsorption entropy ( $\Delta S_{\text{ads}}^{\circ}$ ) were calculated and discussed, which well explained that the synergistic effect between the quaternary ammonium cations and the halide anions greatly influenced the effective inhibiting tendency.

**Keywords:** Quaternary ammonium cationic surfactant; Inhibitor; Acid corrosion; Adsorption; Mechanism

### 1. Introduction

Carbon steel has been widely used as the main alloy in petroleum and gas industries, transmission pipelines, oil production, and refining processes. The wide variety of carbon steel applications is due to its obvious advantages such as low cost, exclusive properties, and excellent mechanical strength. However, corrosion is a major concern, which affects the remarkable characteristics of carbon steel in all its applications and imposes unexpected costs and effects on the economy and also on human health and safety. Despite its relatively limited corrosion resistance, carbon steel is the

largest single class of alloys in use [1–5]. Due to this fact, many attempts have been made to control this undesirable reaction and even entire elimination of it [6–8].

Many chemical processes such as acid descaling or elimination of salt sediments, deposit sand rust (for example in the cleaning of boilers) require the use of mineral acids, especially hydrochloric acid [9,10]. However, in these processes, which are used for metals cleaning or descaling, the corrosive acid can also damage the base metal. Considering this issue, among diverse approaches, the utilization of corrosion inhibitors is attracting considerable attention in preventing an attack from acid species [11]. As a crucial

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placeholder, organic inhibitors, possessing N, O, S, unsaturated bond, as well as aromatic rings can adsorb onto the outward steel surface by physical adsorption (electrostatic interactions between the inhibitor and metal) or by chemical adsorption (by coordinate covalent bonds) and prevent acid corrosion [12]. Besides, organic compounds, diverse surface-active compounds or surfactants, like ionic surfactants [13], non-ionic surfactants [14], and cationic surfactants [15,16]. Due to the presence of the  $-C=N$  group in the cationic surfactant, they should be described as proficient rust preventing inhibitors. They have many advantages such as high inhibition efficiency, inexpensive, low toxicity and ease of manufacturing. This brand of organic corrosion inhibitors is characterized by their high capability to adsorb on a metal interface because of high surface effectiveness [17]. The movement of the surfactant inhibitors from the bulk solution to the interface is governed by their hydrophobic chain length; in addition, hydrophobic tails make barrier film which segregates the surface of the metal from the corrosive solution. Generally, the surfactants head group contains an electron-rich functional group, which participates in the adsorption process with the metal vacant d-orbital.

Among the many cationic surfactants available, quaternary ammonium inhibitors are important as inhibitor additives because of their relatively outstanding inhibition efficiency [18–20]. The effect functional groups and halide ions of quaternary ammonium inhibitors on the corrosion of iron and steel have been studied extensively. However, the synergistic effect between the organic cations and the halide anions is considered to be an important factor in inhibiting action on metal corrosion, but this effect is scarcely discussed [21]. Thus, this paper evaluated that four quaternary ammonium cationic surfactants, cetyl-trimethyl ammonium fluorine (CTAF), cetyl-trimethyl ammonium chlorine (CTAC) [22,23], cetyl-trimethyl ammonium bromine (CTAB) [24,25] and cetyl-trimethyl ammonium iodine (CTAI) were purchased as carbon steel corrosion inhibitors and discussed the synergistic effect between the organic cations and the

halide anions on inhibiting tendency by thermodynamics methods.

## 2. Experimental setup

### 2.1. Materials

The chemical structures of the studied quaternary ammonium halides inhibitors are shown in Fig. 1. These inhibitors were analytical grade reagent and purchased from Tianjin kemiu chemical Reagent Co., Ltd. Alcohol and acetone obtained from Chengdu Aikeda Chemical Reagent Co. Ltd., was of analytical grade with a purity of 99.8%. The corrosion tests were done using carbon steel samples having the following composition: C 0.693%, Si 0.043%, Mn 1.050%, P 0.069%, Cr 0.058%, Ni 0.074%, Al 0.036%, S 0.290%, Cu 0.167%, V 0.004%, W 0.001%, Mo 0.0143% and the balance iron. By considering the carbon content of the samples, it could be classified as high carbon steel. Before doing each experiment, the carbon steel surface was abraded by a series of emery papers (grade 400–1,200), degreased and cleaned in an ultrasonic bath with ethanol and acetone, and washed with distilled water [26].

### 2.2. Solutions preparation

The HCl solution was considered as the most widely corrosive media in many fields, and the desired concentration of HCl in the experiment was determined by dilution of HCl with a purity of 37% using distilled water. The four inhibitors with different concentrations ranging from 0.1 to 5.0 mg L<sup>-1</sup> were added to the prepared HCl [27].

### 2.3. Weight loss measurements

Weight loss experiments were run on test specimen according to the ASTM designation G 31–72 [20]. The pre-cleaned and weighed coupons were hanged in beakers

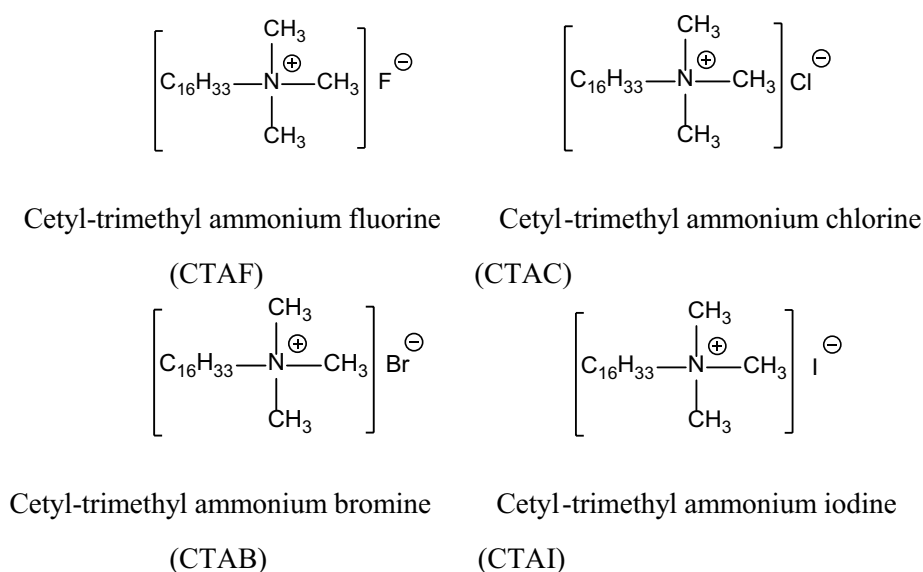


Fig. 1. Chemical structure of quaternary ammonium halides.

containing 250 mL test solution. To avoid galvanic and crevice corrosion the specimens were loosely tied with the nylon threads. The absence and presence of various concentrations of the inhibitors CTAF, CTAC, CTAB and CTAI for 2 h at 303, 323 and 343 K in a thermo stated water bath. To calculate the weight loss, the mild steel coupons were retrieved from test solution after 2 h, cleaned following ASTM designation G1-90 [28], air-dried, and reweighed. The weight of the specimens before and after immersion was recorded by an electronic balance (0.1 mg accuracy). All tests were done in aerated unstirred solutions.

### 3. Results and discussion

#### 3.1. Effect of concentration

The values of carbon steel corrosion rate (CR) in the absence and presence of different concentrations of CTAF, CTAC, CTAB, and CTAI were calculated according to the following equation [29]:

$$CR = \frac{W_0 - W_t}{S \cdot t} \quad (1)$$

where  $W_0$  and  $W_t$  are respectively the mass values of carbon steel sheet before and after immersion in the corrosive solution (g),  $A$  is the total area of carbon steel sheet ( $m^2$ ),  $t$  is the corrosion time (h) and CR is the corrosion rate ( $g\ m^{-2}\ h^{-1}$ ). To calculate the values of surface coverage ( $\theta$ ) and inhibition efficiency ( $\eta\%$ ), the following equations were used [30]:

$$\theta = \frac{CR_{\text{uninhibit}} - CR_{\text{inhibit}}}{CR_{\text{uninhibit}}} \quad (2)$$

$$\eta\% = \frac{CR_{\text{uninhibit}} - CR_{\text{inhibit}}}{CR_{\text{uninhibit}}} \times 100 \quad (3)$$

In these equations,  $CR_{\text{uninhibit}}$  and  $CR_{\text{inhibit}}$  are the values of carbon steel corrosion rates in uninhibited and inhibited solutions, respectively. In Table 1, the values of CR,  $\theta$  and  $\eta\%$  after 2 h immersion in the weight loss solutions without and with different concentrations of CTAF, CTAC, CTAB, and CTAI at 323 K were listed.

The values of percentage inhibition efficiency and corrosion rate obtained from weight loss method at different concentrations (from 0.1 to 20.0  $mg\ L^{-1}$ ) of the inhibitors at 323 K are summarized in Table 1, it was clear from the table that the inhibition efficiency increased with the increase of inhibitor concentrations. Hence, the corrosion rate was concentration-dependent. At low inhibitor concentrations, the adsorption took place by binding to the hydrophobic region as seen in Fig. 2a. In other words, a mono disordered layer could be formed. This adsorption was a competitive one because the inhibitor displaces progressively the water molecules and other ions adsorbed on the metal surface. When inhibitor concentration increased, an un-complete packing layer of the inhibitor molecules was formed in which adsorption took place as a result of inter-hydrophobic chain interactions which clear in Fig. 2b. In other words, the increase in inhibition efficiency observed at higher

Table 1

Corrosion parameters of mild steel following 2 h in 5% HCl solution in the absence and presence of various concentrations of four inhibitors at 323 K

Inhibitor	Concentrations ( $mg\ L^{-1}$ )	CR ( $g\ m^{-2}\ h^{-1}$ )	$\theta$	$\eta\%$
CTAF	0.1	8.5251	0.48	48.00
	0.5	7.2463	0.56	55.80
	1.0	6.1479	0.63	62.50
	2.5	5.0003	0.70	69.50
	5.0	3.9674	0.76	75.80
	10.0	3.2115	0.81	80.51
	20.0	1.9923	0.87	87.00
CTAC	0.1	7.3775	0.55	55.00
	0.5	6.2299	0.62	62.00
	1.0	5.0822	0.69	69.00
	2.5	4.1806	0.75	74.50
	5.0	3.2788	0.80	80.00
	10.0	2.3172	0.85	85.23
	20.0	1.8274	0.89	88.91
CTAB	0.1	6.1479	0.63	62.50
	0.5	5.0823	0.69	69.00
	1.0	3.8035	0.77	76.80
	2.5	3.2461	0.80	80.20
	5.0	2.2132	0.87	86.50
	10.0	1.7297	0.90	89.50
	20.0	1.3192	0.92	92.00
CTAI	0.1	5.0823	0.69	69.01
	0.5	4.0576	0.75	75.00
	1.0	2.8748	0.82	82.28
	2.5	1.9345	0.88	88.07
	5.0	1.5606	0.90	90.38
	10.0	1.3515	0.92	91.82
	20.0	1.0711	0.93	93.50

inhibitor concentrations indicated that more inhibitor molecules were adsorbed on the metal surface, thus providing wider surface coverage [31]. Meanwhile, at the overdose concentration (at maximum inhibition efficiency obtained), the interspace area between the adsorbed inhibitor molecules on the surface could be lesser than the area of the inhibitor molecules. So the inhibitor molecules turned out to form the double layer adsorption as shown in Fig. 2c. It could be inferred from the data shown in Table 1 that, the inhibition efficiency became nearly constant starting from 10.0  $mg\ L^{-1}$ . This concentration could be used as the up limit through this study.

Table 1 also shows that at the same inhibitor concentration, the inhibition efficiency of four inhibitors followed the order CTAI > CTAB > CTAC > CTAF. Hence, CTAI had a more inhibiting effect for iron corrosion in 5.0% HCl solution than CTAF, CTAC, and CTAB. This difference could be attributed to molecular structures of organic inhibitors, especially the adsorption orientation of the inhibitors on the metal surface. It has been reported that the adsorption

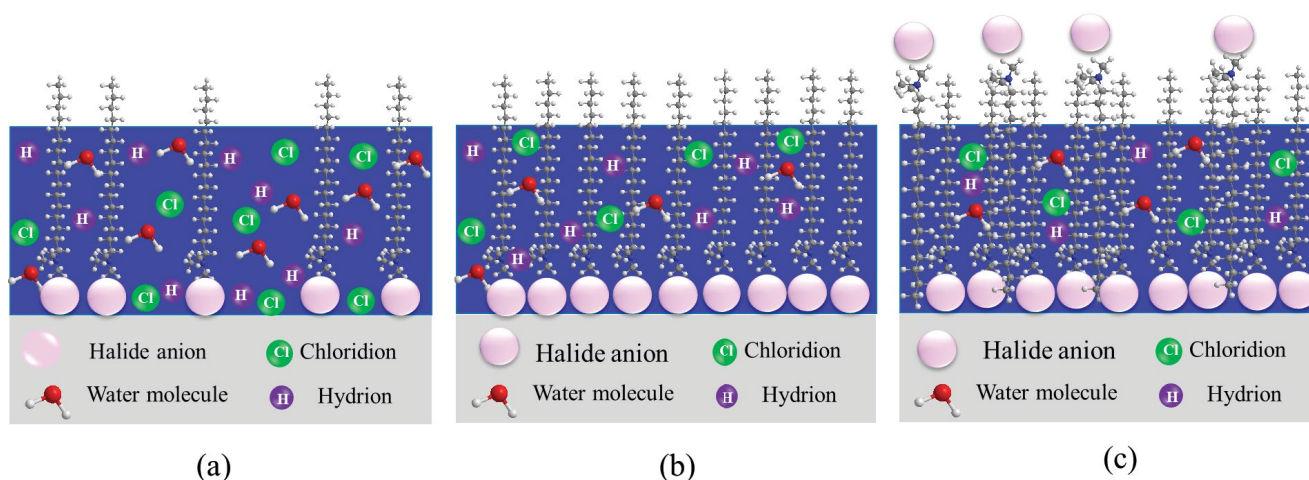


Fig. 2. Adsorption of inhibitor on the surface (a) low concentration, (b) high concentration, and (c) overdose concentration.

was dependent on the following physicochemical properties of the inhibitor molecule, such as steric factors, functional groups, electron density (i.e. charge distribution) at the donor atoms and p orbital character of donating electrons, and on the natures of substrate metals and the type of interaction between organic molecules and the metallic surface as well [32]. In other words, the efficiency of an organic compound as corrosion inhibitor depended not only on the characteristics of the environment in which it acted, the nature of the metal surface and electrochemical potential at the interface but also on the structure of the inhibitor itself, which included the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface.

Four inhibitors, CTAF, CTAC, CTAB, and CTAI, possessed different halide ions with the same charges even though their hydrophobic and hydrophilic groups were the same. Hence, the difference in the inhibition efficiency produced by the four inhibitors could be mainly attributed to the discrepancy of the halide ions. [33]. the ionic radius of electron cloud increased from  $F^-$  to  $I^-$  ( $F^- = 71$  pm,  $Cl^- = 99$  pm,  $Br^- = 114$  pm,  $I^- = 133$  pm), which indicated that  $I^-$  was easily deformed and therefore promoted the strong adsorption on the metal surface, yet this strong adsorption of iodide ions was responsible for the synergistic effect of iodide ions, in attraction with cations. It was apparent then that the effects of iodide ions were not due to electrostatic effects alone, but some covalent bonding to the metal must be involved. The large size and ease of polarizability of iodide facilitated electron pair bonding.

### 3.2. Effect of HCl concentration

The effect of HCl concentration in the range of 0.5%–15.0% on the corrosion rate of carbon steel was investigated in presence of the prepared inhibitor with  $5.0$  mg  $L^{-1}$  at 323 K. The corrosion parameters extracted from weight loss technique are shown in Table 2 for CTAF, CTAC, CTAB, and CTAI. In Table 2, it is noticed that with increasing HCl

concentration in the solution, the inhibition efficiency of the used inhibitors was decreased. Whereas, increasing the HCl concentration from 0.5% to 15.0% caused the corrosion rate of an inhibitor to increase. This was because the pH of the solution decreased with the rise in HCl concentration, the concentration of the hydrogen ion in the corrosion medium increased and a large number of hydrogen ions and inhibitor molecules competed for adsorption on the corrosion matrix layer, this reduced the adsorption effectiveness of inhibitor molecules on the steel surface. Therefore, the corrosion rate increased under HCl concentration effect. In addition, Table 3 also shows that at the same concentration of HCl solution, the inhibition efficiency of four inhibitors followed the order  $CTAI > CTAB > CTAC > CTAF$ , which indicated the highest adsorption and inhibition efficiency of CTAI.

### 3.3. Effect of temperature

In order to investigate the effect of temperature in the range of 303–343 K on the corrosion rate of carbon steel in 5% HCl solution having the same concentration ( $5.0$  mg  $L^{-1}$ ) of four inhibitors. The corrosion parameters extracted from the weight loss technique are shown in Table 2, it was noticed that increasing the temperature from 303 to 343 K caused the corrosion rate of an inhibitor to increase. Whereas, the inhibition efficiency presented an opposite tendency. This could be attributed to the dissolution rate of the carbon steel surface. The prevailing carbon steel coupon's dissolution on the metal surface at higher heat ranges resulted in decreasing the inhibition efficiency by increasing temperature. Hence, the physical adsorption process was preferred for the introduced inhibitors in this work since the adsorption effectiveness decreased with the increase of heat range [34]. This phenomenon was also explained based on the effect of halide ions in the used inhibitor. Therefore, under the temperature effect, as the ionic radius of the electron cloud increased, the corrosion rate values increased. The obtained results in this study as reported in Table 2 are in agreement with most studies previously reported in the literature [35,36].

The  $\log CRs$   $1/T$  could be represented as a straight-line function in Fig. 3. All of the linear regression coefficients ( $R^2$ )

Table 2

Corrosion parameters of mild steel following 2 h in different HCl concentration in the presence of four inhibitors with 5.0 mg L<sup>-1</sup> at 323 K

Inhibitor	HCl concentrations (%)	CR (g m <sup>-2</sup> h <sup>-1</sup> )	θ	η (%)
CTAF	0.5	2.5774	0.84	84.28
	2.5	3.6015	0.78	78.06
	5.0	3.9674	0.76	75.80
	10.0	7.2146	0.56	56.20
	15.0	8.4198	0.48	48.32
CTAC	0.5	1.7765	0.89	89.20
	2.5	2.7813	0.83	83.12
	5.0	3.2788	0.80	80.00
	10.0	6.4219	0.62	61.56
	15.0	7.9464	0.52	52.48
CTAB	0.5	1.2974	0.92	92.17
	2.5	1.6466	0.90	90.08
	5.0	2.2132	0.87	86.50
	10.0	4.6153	0.72	72.17
	15.0	5.8344	0.65	64.85
CTAI	0.5	0.5863	0.96	96.47
	2.5	0.7109	0.96	95.72
	5.0	1.5606	0.93	90.38
	10.0	4.0467	0.76	75.64
	15.0	4.9738	0.70	70.08

were almost equal to 1, which manifested that the adsorption process of the additives of CTAF, CTAC, CTAB, and CTAI on the steel surface in acid solution complied with the Arrhenius adsorption [37].

The apparent activation energy ( $E_a$ ) during the dissolution of the steel sheets could be evaluated from the Arrhenius Eq. (4) [38]:

$$\log CR = -\frac{E_a}{2.303RT} \times \log \lambda \quad (4)$$

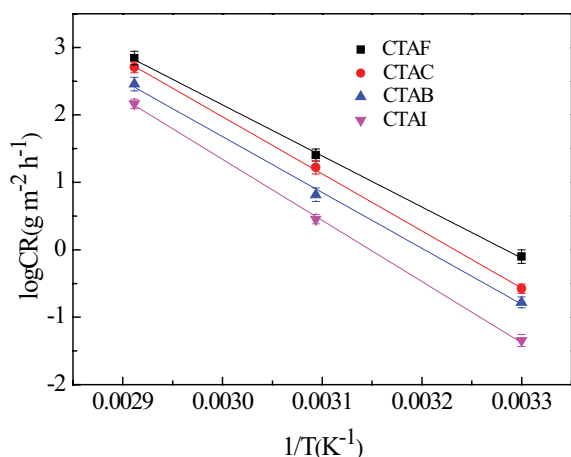


Fig. 3. Arrhenius plot of  $\ln W_{\text{corr}}$  vs.  $1/T$  for carbon steel corrosion in 5% HCl in the presence of 5.0 mg L<sup>-1</sup> of CTAF, CTAC, CTAB, and CTAI.

where  $E_a$  is the apparent activation energies for the corrosion (kJ mol<sup>-1</sup>),  $T$  is the absolute temperature (K),  $R$  is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>).  $\lambda$  is a constant related to the Arrhenius pre-exponential factor. Other symbols are the same as previous equations. The logarithm of corrosion rate of the steel plates could be represented as a straight-line function of  $1/T$  (Arrhenius equation) in Fig. 3.

Fig. 3 shows the Arrhenius plot of carbon steel corrosion in 5.0% HCl in the presence of 5.0 mg L<sup>-1</sup> of CTAF, CTAC, CTAB, and CTAI. Out of these Arrhenius plots,  $E_a$  values were calculated and gathered in Table 3. From the obtained results, it was noticed that the  $E_a$  values for the corrosion process of carbon steel in the HCl solutions containing 5.0 mg L<sup>-1</sup> of CTAF, CTAC, CTAB and CTAI are 46.2, 47.1, 49.5 and 50.2 KJ mol<sup>-1</sup>. Therefore, the  $E_a$  values of CTAI was the largest compared to other members in the inhibitors studied, indicating that CTAI among four inhibitors was the most easily to adsorb on the steel surface. However, the  $E_a$  values for four inhibitors were within the range of physical adsorption (less than 80 KJ mol<sup>-1</sup>). As reported by previously workers, Arrhenius equation proved that the corrosion rate depended on the applied temperature. Physical adsorption was predominant over chemical adsorption owing to the decrease of corrosion rate with temperature [39].

#### 3.4. Adsorption isotherm and thermodynamic parameters

In order to elucidate the adsorption mode of inhibitors on the carbon steel surface, the equilibrium constant and thermodynamic parameters of the adsorption process were calculated using the data obtained by using a weight-loss

method. To deduce the adsorption isotherm, the surface coverage values were fitted as a function of inhibitors concentration. Among Langmuir, Temkin and Frumkin isotherms, Langmuir showed the best fit with the WL results. Langmuir isotherm obeys the following equation [40].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (5)$$

Table 3  
Corrosion parameters of mild steel following 2 h in 5% HCl solution in the presence of four inhibitors with 5.0 mg L<sup>-1</sup> at temperatures from 303 to 343 K

Inhibitor	T (K)	CR (g m <sup>-2</sup> h <sup>-1</sup> )	θ	η (%)
CTAF	303	0.8803	0.81	80.50
	323	3.9674	0.76	75.80
	343	16.9255	0.70	69.60
CTAC	303	0.5598	0.88	87.60
	323	3.2788	0.80	80.00
	343	14.8098	0.73	73.40
CTAB	303	0.4424	0.90	90.20
	323	2.2132	0.87	86.50
	343	11.8033	0.79	78.80
CTAI	303	0.2618	0.94	94.20
	323	1.5606	0.90	90.38
	343	8.7968	0.84	84.20

where C<sub>inh</sub> is the inhibitors concentration (mmol L<sup>-1</sup>), θ is the surface coverage and K<sub>ads</sub> is the adsorptive equilibrium constant (L mmol<sup>-1</sup>). Fig. 4 show Langmuir adsorption plots for the four inhibitors on carbon steel surface, was obtained at temperatures 303, 323 and 343 K. As shown in the figure, the values of linear correlation coefficients and slopes are very close to 1, approving the Langmuir model of adsorption. The values of K<sub>ads</sub> were calculated from the intercepts of the straight lines and are listed in Table 4.

As can be seen in the table, the values of K<sub>ads</sub> for CTAI were the highest compared with other members in the studied inhibitors, reflecting the strongest adsorption of CTAI on the carbon steel surface. It was observed that by increasing temperature, the value of K<sub>ads</sub> decreased, which demonstrated the rise in solution temperature leads to more agitation and consequently desorption of some inhibitor molecules from the metal surface [41,42]. The obtained values of K<sub>ads</sub> for CTAF, CTAC, CTAB and CTAI at 303 K were 195.69, 231.48, 411.52 and 625.00 L mmol<sup>-1</sup>, respectively.

The value of K<sub>ads</sub> can be used to calculate the standard free energy of the inhibitor adsorption according to the following equation [43]:

$$\Delta G_{ads}^{\circ} = -RT \ln 55.5 K_{ads} \quad (6)$$

where ΔG<sub>ads</sub><sup>°</sup> are the standard free energy (kJ mol<sup>-1</sup>) and 55.5 is the molar concentration of water in the solution (mol L<sup>-1</sup>). The calculated values of ΔG<sub>ads</sub><sup>°</sup> for CTAF, CTAC, CTAB, and CTAI are also listed in Table 4. The negative sign of ΔG<sub>ads</sub><sup>°</sup> values demonstrated that the adsorption of the inhibitors

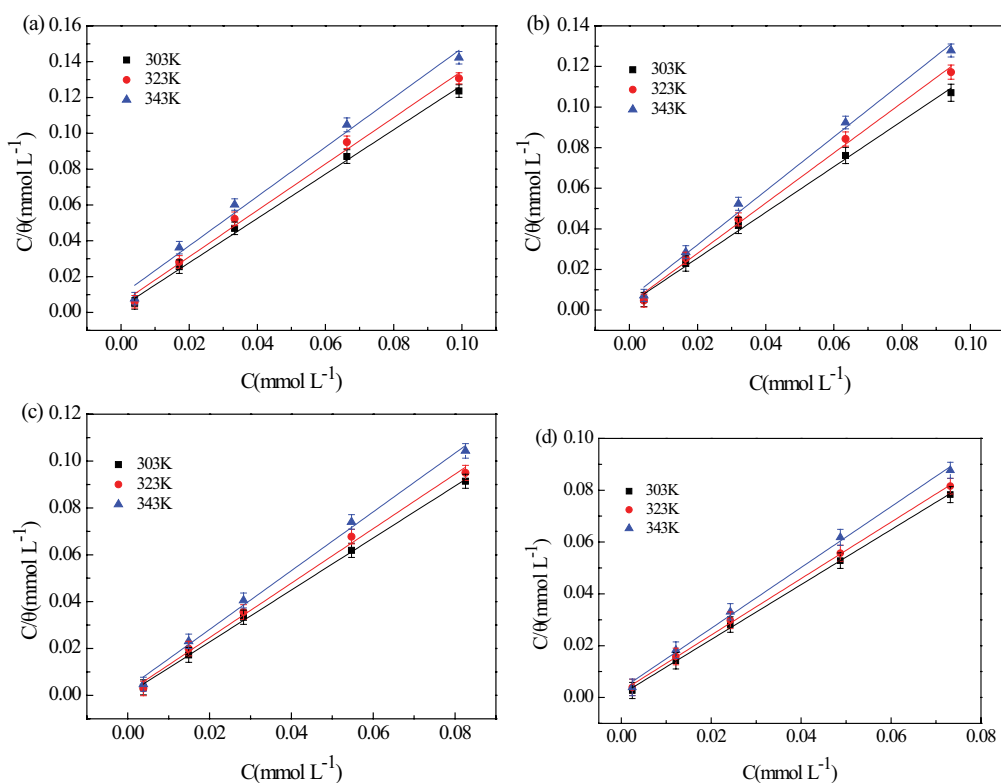


Fig. 4. Langmuir adsorption isotherm model for CTAF (a), CTAC (b), CTAB (c) and CTAI (d) on carbon steel surface at temperatures 303, 323 and 343 K.

Table 4

Standard thermodynamic and equilibrium parameters for the adsorption of CTAF, CTAC, CTAB, and CTAI on carbon steel surface in 5.0% HCl at temperatures 303, 323, and 343 K

Inhibitor	T (K)	R-Square	Slope	$K_{ads}$ (L mmol <sup>-1</sup> )	$\Delta G_{ads}^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta H_{ads}^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta S_{ads}^{\circ}$ (J mol <sup>-1</sup> K <sup>-1</sup> )
CTAF	303	0.9965	1.2115	195.69	-23.41		45.12
	323	0.9926	1.2806	139.66	-24.05	-9.74	44.30
	343	0.9868	1.3699	91.99	-24.33		42.59
CTAC	303	0.9960	1.1167	231.48	-23.83		45.35
	323	0.9954	1.2209	197.23	-24.98	-10.09	46.08
	343	0.9929	1.3206	145.77	-25.66		45.39
CTAB	303	0.9988	1.0883	411.52	-25.28		42.57
	323	0.9959	1.1379	290.69	-26.02	-12.39	42.21
	343	0.9954	1.2391	221.72	-26.86		42.19
CTAI	303	0.9994	1.0441	625.00	-26.34		38.49
	323	0.9988	1.0824	446.42	-27.17	-14.67	38.69
	343	0.9967	1.1654	316.45	-27.87		38.47

on the carbon steel surface took place spontaneously. On the one hand, the  $|\Delta G_{ads}^{\circ}|$  values were 20 kJ mol<sup>-1</sup> or lower, implying that inhibitor was physically adsorbed by the electrostatic force between the inhibitor molecule and the active site of the metal surface [44,45]. On the other hand, the  $|\Delta G_{ads}^{\circ}|$  values were 40 kJ mol<sup>-1</sup> or higher, it was proved chemical adsorption in virtue of covalent bond between inhibitor molecules and the empty orbit of the metal by the shared charge or the transferred charge. However, the values of  $|\Delta G_{ads}^{\circ}|$  for CTAF, CTAC, CTAB, and CTAI in the range between 20 and 40 kJ mol<sup>-1</sup>, indicating that the adsorption process involved both chemisorption and physisorption [46]. And the absolute value of Gibbs free energy increases with increasing.

Fig. 5 shows the plot of  $\log K_{ads}$  vs.  $1/T$ , which can be used to obtain the standard enthalpy change ( $\Delta H_{ads}^{\circ}$ ) and the standard entropy change of adsorption ( $\Delta S_{ads}^{\circ}$ ) using the Van't Hoff equation [13]:

$$\log K_{ads} = \frac{-\Delta H_{ads}^{\circ}}{2.303RT} + \frac{-\Delta S_{ads}^{\circ}}{2.303R} - \log 55.5 \quad (7)$$

The values of  $\Delta H_{ads}^{\circ}$  and  $\Delta S_{ads}^{\circ}$  are calculated from the slope and intercept of the straight lines in Fig. 3 Thermodynamic parameters,  $\Delta H_{ads}^{\circ}$  and  $\Delta S_{ads}^{\circ}$  can also be calculated from the basic thermodynamic equation [47]:

$$\Delta G_{ads}^{\circ} = \Delta G_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \quad (8)$$

The obtained values from both Fig. 5 were in good agreement and listed in Table 4. The negative sign of  $\Delta H_{ads}^{\circ}$  indicated the exothermic nature of the adsorption process, confirming the desorption of some inhibitor molecules with increasing the solution temperature, which leads to a decrease in  $K_{ads}$  values. Generally, in an adsorption process, endothermic nature specifies chemisorption, but exothermic nature indicates either physisorption or chemisorption. For physisorption, the value of  $\Delta H_{ads}^{\circ}$  was usually in the

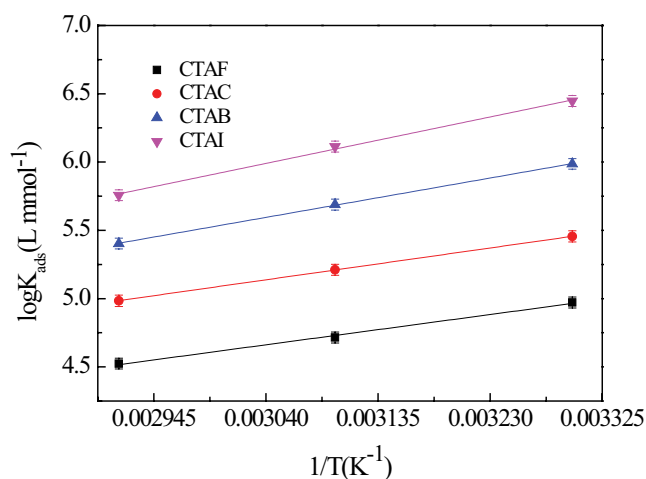


Fig. 5. Plots of  $1/T$  vs.  $\ln K_{ads}$  for adsorption of four inhibitors on the steel surface in 5.0% HCl solution at temperatures 303, 323 and 343 K.

range  $-10$  to  $-40$  kJ mol<sup>-1</sup>, while the standard enthalpy of a chemisorption process often exceeded  $-100$  kJ mol<sup>-1</sup>. As seen in Table 4, the values of  $\Delta H_{ads}^{\circ}$  (from Van't Hoff equation) for CTAF, CTAC, CTAB and CTAI were respectively  $-9.74$ ,  $-10.09$ ,  $-12.39$  and  $-14.67$  kJ mol<sup>-1</sup>. These values indicated that the adsorption of CTAF, CTAC, CTAB and CTAI on carbon steel surface involved physisorption. With the highest value of  $|\Delta H_{ads}^{\circ}|$ , CTAI could absorb on the steel surface the most tightly compared with other members in the studied inhibitors, which leads to the highest corrosion inhibition. What's more, it was observed that the value of  $\Delta S_{ads}^{\circ}$  in the presence of CTAF, CTAC, CTAB and CTAI was positive value. This indicated that the adsorption process of the inhibitor on the carbon surface was accompanied by increases in entropy. Furthermore, the results in Table 3 show that the positive value of  $\Delta S_{ads}^{\circ}$  increased as the ionic radius of electron cloud increases. These positive values of

the entropy referred to the increment in the randomness during the adsorption of the incorporated inhibitors onto the metal surface. It was observed that  $\Delta S_{\text{ads}}^{\circ}$  values in the presence of the inhibitors were positive signs suggesting an increase of disorder. The increase of entropy was due to the adsorption of only one inhibitor molecule by the replacement of more adsorbed water molecules.

### 3.5. Inhibition mechanism

As reported in the literature, in the HCl solution, the mechanism of corrosion inhibitor has been extensively studied. It is generally accepted that complexation reaction between the synthesized compounds and the  $\text{Fe}^{2+}$  occur on the positive and negative centers on the metal surface which decreases the electrochemical dissolution of the metal to ions in the solution. At first, the  $\text{Cl}^-$  ions from HCl solution and halide ions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ) from four inhibitors are adsorbed on the positively charged metal surface thus changing the charge on the solution side of steel/solution interface from positive to negative. Based on a negatively charged steel surface, the ammonium groups ( $\text{N}^+$ ) are adsorbed on the surface of the steel plate by electrostatic action to form a protective film ad that separates the medium from the metal surface and acts as a protective metal. The adsorption model is shown in Fig. 6.

However, there is a different adsorption capacity on the halide ions from four inhibitors. As noted in the above section, the specific adsorption capacity of CTAI is the strongest compared with CTAF, CTAC, and CTAB. The reason is that the strongest chemisorption of iodide ions on the metal

surface is responsible for the synergistic effect of iodide ions, in attraction with cations. It is apparent then that the effects of iodide ions are due to some covalent bonding to the metal must be involved. The large size and ease of polarizability of iodide facilitate electron pair bonding. In short, the adsorption of inhibitors between the metal and solution interface is usually accepted as the formation of electrostatic or covalent bonding between the adsorbates and the metal surface atoms. In other words, halide ions will adsorb on the metal surface by creating oriented dipoles with their negative ends towards the solution, thus increase the adsorption of the organic cations on the dipoles. Consequently, a positive synergistic effect arises [21].

### 3.6. Comparison of inhibitory efficiencies of some cationic surfactants for carbon steel in HCl solution

The inhibitory efficiency of the prepared quaternary ammonium cationic surfactants for carbon steel corrosion in 5% HCl solution and some of the previously reported surfactants [48,49] are depicted in Table 5. As can be seen in this table the inhibitory efficiencies of the prepared surfactants were comparable to or better than those of previously reported cationic surfactants at the same condition.

## 4. Conclusion

Four quaternary ammonium cationic surfactants, CTAF, CTAC, CTAB, and CTAI, act as good inhibitors for carbon steel corrosion in HCl solution of different concentration were studied at the temperature 303, 323, and 343 K. The

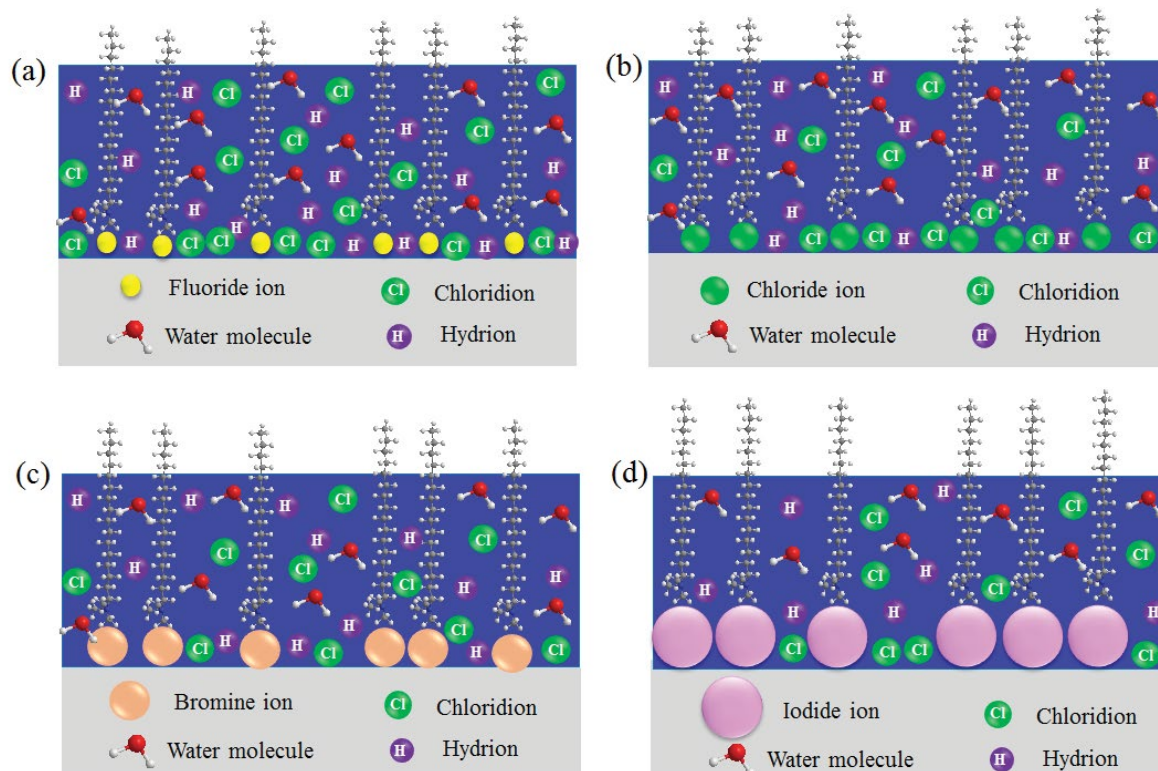


Fig. 6. Adsorption of four inhibitors on the steel surface. (a) CTAF, (b) CTAC, (c) CTAB, and (d) CTAI.



Table 5

Some cationic surfactants investigated as corrosion inhibitors by other authors and this work for carbon steel in 5% HCl (the data obtained by weight loss method)

Inhibitor name	Inhibition efficiency (%)	Reference
Dodecyl-trimethyl ammonium chloride	88.5	[22]
Tetradecyl-trimethyl ammonium chloride	86.2	[22]
Octadecyl-trimethyl ammonium chloride	82.7	[22]
Cetyl-trimethyl ammonium chloride	88.7	[21]
Cetyl-dimethyl-hydroxyethyl ammonium chloride	89.9	[21]
Cetyl-trimethyl ammonium glycine	91.1	[50]
Cetyl-trimethyl ammonium oxalate	86.7	[51]
Cetyl-trimethyl ammonium malonate	83.3	[51]
Cetyl-trimethyl ammonium succinate	81.5	[51]
Cetyl-trimethyl ammonium glutarate	80.0	[51]
Cetyl-trimethyl ammonium adipate	78.5	[51]
Cetyl-trimethyl ammonium sebacate	75.9	[51]
Cetyl-trimethyl ammonium fluorine	87.9	This work
Cetyl-trimethyl ammonium chlorine	88.9	This work
Cetyl-trimethyl ammonium bromine	92.0	This work
Cetyl-trimethyl ammonium iodine	93.5	This work

results showed that the type of halide ions of quaternary ammonium halides inhibitors greatly influenced the inhibition efficiency. The inhibition efficiencies of these inhibitors followed the order CTAI > CTAB > CTAC > CTAF under the same experimental conditions. Based on weight loss results, it was illustrated that the adsorption of CTAF, CTAC, CTAB, and CTAI obeyed Langmuir adsorption isotherm. Through the thermodynamic study of the four corrosion inhibitors, it was found that CTAI had a more inhibiting effect for iron corrosion in HCl solution than CTAF, CTAC, and CTAB in view of the most strong adsorption ability of iodide anions among halide ions. Overall, it was concluded that the synergistic effect between the quaternary ammonium cations and the halide anions greatly influenced the effective inhibiting tendency.

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