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Corrosion inhibition of mild steel in hydrochloric acid solutions via cetyl trimethyl ammonium bromide inhibitor

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ABSTRACT

Cetyl trimethyl ammonium bromide (CTAB) has been studied as a corrosion inhibitor of mild steel in 0.1 and 0.5 M HCl solutions using weight loss, polarization and electrochemical Impedance spectroscopy techniques (EIS). The results showed increasing the inhibition efficiency with increasing CTAB concentrations and decreasing with increasing the temperature. CTAB adsorption on the steel surface obeyed Langmuir adsorption isotherm. Potentiodynamic polarization curves showed that CTAB acted as a cathodic inhibitor. This supported by the impedance measurements which illustrated changing in charge transfer resistance and double layer capacitance, indicating adsorption of CTAB on the surface. The calculated parameters proved that the adsorption mechanism is physisorption and chemisorptions.

KEYWORDS

Inhibitor;
Mild steel;
EIS;
Potentiostatic;
Weight loss;
Acid inhibition.

INTRODUCTION

The carbon steel is used as essential part in the manufacturing of installations used in the petroleum and other industries. Corrosion is a common phenomenon in industries, and it attracts considerable interest because of its hazardous nature on metals[1]. Acids are widely used in industries such as pickling, cleaning, descaling, oil-well acid in oil recovery, and the petrochemical processes, which leads to corrosive attack of metals[2-4]. So, the use of inhibitors is one of the most practical methods to reduce the corrosive attack on metallic materials[5,6]. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration and temperature, the presence of dissolved organic and/or inorganic substances and on the type of metallic material exposed to the action of the acidic solution. Also, cost, toxicity, and availability are important factors in the selection and utilization of these inhibitors. Most of the inhibitors are organic molecules[7]; however, inorganic molecules[8] and polymeric materials[9] are also used. The organic inhibitors decrease the corrosion rate by adsorbing on the metal surface and blocking the active sites by displacing water molecules and form a compact barrier film on the metal surface[10-17]. It has been reported that quaternary ammonium compounds (surfactants) are important as inhibitor additives in hydrochloric acid. Many mechanisms have been proposed for the inhibition of metal corrosion by organic inhibitors[18–20].

The present work was undertaken to investigate the corrosion inhibition behavior of Cetyl trimethyl ammonium bromide (CTAB) on mild steel in 0.1 and 0.5 M HCl solutions. The inhibition efficiency of this additive will be discussed in relation to the effect of the corresponding structure, atom of active center and substituted halide (Br), in attempting to explain the way whereby corrosion resistance is improved. For this purpose, the behavior of carbon steel in HCl acid solutions in the absence and presence of the inhibitor was studied using weight loss, Tafel polarization and electrochemical Impedance spectroscopy (EIS) techniques.

EXPERIMENTAL

Weight loss technique

Experiments were performed using low carbon steel with the following chemical composition (wt.%): C: 0.06, Mn: 0.7, Si: 0.06, S: 0.012, P: 0.001, V: 0.005, Ni: 0.015, Cr: 0.004, Mo: 0.002, Cu: 0.02 and iron is the remainder and with size (2 cm × 4 cm × 0.3 cm). For all experiments, the surface pretreatment was carried out by polishing with SiC emery papers of different grades (400, 800, 1000 and 1200), rinsed with distilled water, and degreased in alkaline degreaser for 5 minutes at 70 °C and finally dried using a stream of air at room temperature. The acidic solutions 0.1 and 0.5 M HCl were prepared by dilution of analytical grade 37% HCl using triply distilled water. The inhibitor used, namely CTAB is a surfactant with the formula ($C_{16}H_{33})N(CH_3)_3Br$). All solutions were prepared using distilled water.

Inhibition efficiencies (IE%) of the inhibitor at fixed temperature and at different concentrations were calculated from weight loss values in the absence and presence of the inhibitor. Moreover, inhibition efficiencies (IE%) were also estimated at a fixed inhibitor concentration and at different temperatures. The effect of the temperature change in the range of 20– 40 °C (293 – 313 K) on the performance of the inhibitor and the effectiveness of the inhibitor at higher acid strength were also studied. The samples were immersed in 0.1 or 0.5 M HCl solution containing different concentrations of inhibitors for 24 hrs. Samples were weighed before and after immersion and the difference in weights were determined. The percentage inhibition efficiency (IE %) and the degree of surface coverage (θ) was calculated from the following equations:

$$\text{IE \%} = (W_0 – W / W_0) \text{ X } 100 \qquad (1)$$

$$\theta = W_0 – W / W_0 \qquad (2)$$

Where; W_0 and W are the weights loss of mild steel in blank solution and in the presence of the inhibitor, respectively.

The corrosion rate “CR” was calculated from the following equation:

$$\text{CR} = \frac{W_1 - W_2}{ST} \qquad (3)$$

Where; W_1 and W_2 are the weights of the specimen before and after in mg, S (cm^2) is the total area of the specimen and T (hr) is the immersion time. The weight loss data were made after 24 hrs of immersion.

Potentiodynamic polarization measurements

Electrochemical measurements were carried out in a conventional three - electrode cell; platinum sheet and saturated calomel electrode (SCE) were used as a counter and reference electrodes, respectively. The potentiodynamic current – potential curves were recorded by changing the electrode potential automatically from - 0.50 to + 0. 50 V (SCE) and at a scan rate of 10 mV sÎ^1 using Iviumstat instrument (supplied by Ivium technologies, Eindhoven, Netherlands). The Ivium stat software can be used to control Ivium stat instrument, by means of a personal computer (PC). Polarization experiments were measured after 24 hrs of immersion in the test solution. Before recording the polarization curves, the working electrode was maintained at the open circuit potential for ~15 min. until a steady state was obtained. The mild steel surface was exposed to various concentrations of CTAB in 0.1 and 0.5 M HCl at a fixed temperature. In another batch of experiments, the measurements were carried out at a fixed concentration and at different temperatures.

Tafel plots were illustrated by plotting E Vs log I. Corrosion Potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic slopes (β_c and β_a) were calculated according to the well known procedures. The inhibition efficiency (IE%) was calculated using the following equation Inhibition Efficiency:

$$\text{IE \%} = (I_0 – I / I_0) \times 100 \qquad (4)$$

Where I_0 and I are the corrosion current density without and with the inhibitor, respectively.

Electrochemical impedance measurements

The EIS spectra were recorded at the open circuit potential (OCP) after immersion the electrode for ~15 min in the test solution. EIS tests were carried out in the frequency range from 0.1 to $6x10^4$ Hz. The impedance diagrams were plotted in the Nyquist representation. Charge transfer resistance (R_{ct}) values were obtained by subtracting the high-frequency impedance. The percentage inhibition efficiency (IE%) was calculated from the following equation:

$$\text{IE\%} = (R_p - R'_p / R_p) \times 100 \qquad (5)$$

Where; R'_p and R_p are the polarization resistance of mild steel with and without inhibitor, respectively.

RESULTS AND DISCUSSION

Weight loss measurements

The corrosion behavior of a metal in aqueous environment is characterized by measuring the weight loss of a specimen after exposure to corrosive media. The weight loss method is usually preferred because the quantity measured is directly related to the extent of corrosion and does not rely on any assumptions about reactions occurring during corrosion. The weight loss technique was employed as the chemical testing technique to evaluate the influence of inhibitor compounds on the corrosion of low carbon steel in 0.1M and 0.5 M HCl solution at different temperatures 20- 40 °C (293 – 313 K).

Effect of concentration and temperature on the corrosion rate and inhibition efficiency

The results of the gravimetric determination of carbon steel in different acid concentrations (0.1 and 0.5 M HCl) operated at different temperature such as corrosion rate (CR) and inhibition efficiency (IE %) without and with addition of CTAB inhibitor are summarized in TABLES 1-2 and Figures 1-2, respectively. As shown from these tables and figures, at a fixed CTAB concentration, by increasing the tem-

TABLE 1 : Corrosion rates of low carbon steel specimen in 0.1M HCl in the absence and presence of different concentrations of CTAB at each temperature

T(K)	Corr. Rate ($mg.cm^{-2}.h^{-1}$)					
	0 ppm	3 ppm	4 ppm	5 ppm	6 ppm	7 ppm
293	0.159879	0.048844	0.037631	0.026968	0.025523	0.018987
298	0.161048	0.060883	0.046161	0.037149	0.033434	0.025385
303	0.162287	0.079458	0.060195	0.053866	0.049807	0.036874
308	0.163387	0.092529	0.07705	0.068932	0.05992	0.050633
313	0.164626	0.104018	0.097895	0.088539	0.078013	0.069345

TABLE 2 : Corrosion rates of low carbon steel specimen in 0.5 M HCl in the absence and presence of different concentrations of CTAB at each temperature

T(K)	Corr. Rate ($mg.cm^{-2}.h^{-1}$)					
	C_{inh} 0 ppm	5 ppm	10 ppm	15 ppm	20 ppm	25 ppm
293	0.647083	0.18437	0.133187	0.098445	0.067006	0.043822
298	0.672812	0.25454	0.194001	0.158916	0.133462	0.098376
303	0.74484	0.383462	0.313773	0.282058	0.232595	0.196753
308	0.785636	0.500826	0.411392	0.35842	0.306824	0.272427
313	0.826912	0.613718	0.54052	0.454871	0.395363	0.356976

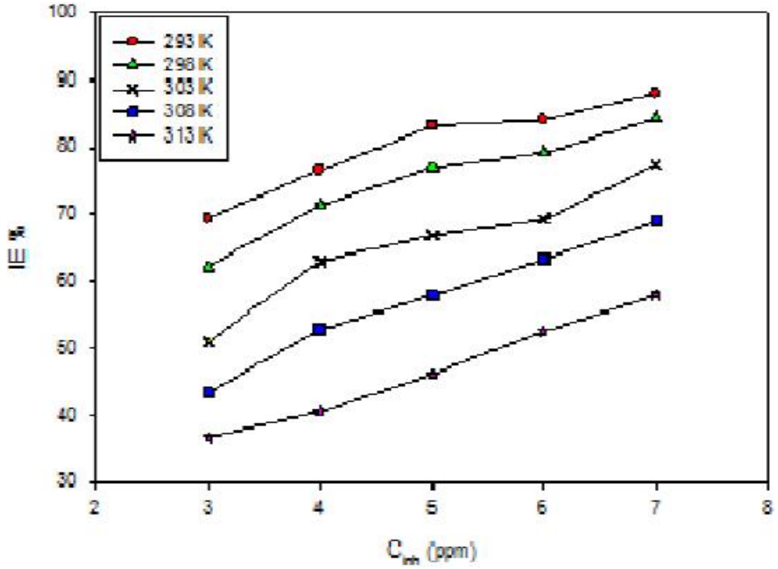

Figure 1 : Variation of IE (%) with a constant concentration of CTAB at different temperatures in 0.1M HCl solution

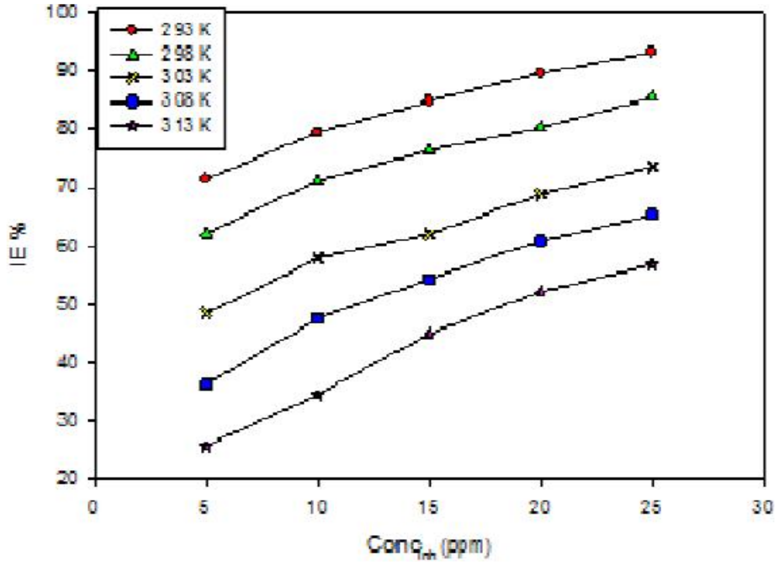

Figure 2 : Variation of IE (%) with with a constant concentration of CTAB at different temperatures in 0.5 M HCl

perature, the corrosion rate of carbon steel increased. On the other hand, a remarkable decrease in the carbon steel corrosion rate was observed with increasing the concentration of inhibitor at each studied temperature. This means that the presence of CTAB inhibitor retards the corrosion of carbon steel in 0.1M and 0.5 M HCl solutions. Moreover, the results reveal that the CR of carbon steel was reduced in the presence of the inhibitor compared with that in the blank acid solution. Also, corrosion rate increases with increasing temperature both in the absence and in the presence of the inhibitor. The rate of all electrochemical processes increases with increasing the temperature as well influences adsorption equilibrium and kinetics. It can be seen that the corrosion rate increases and the inhibition efficiency decreases with temperature in the absence and presence of inhibitor. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between two processes at a particular temperature. With temperature increase, the equilibrium between adsorption and desorption processes is shifted to a higher desorption rate than adsorption until equilibrium is established again at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperature.

It is observed that IE (%) increases with increasing in the concentration of inhibitor and at the same time decreases with increasing in temperature in different HCl concentration solutions. It is illustrated that CTAB has good inhibition efficiency (IE), as the concentration of CTAB increases the inhibition efficiency increases, i.e. 3 ppm of CTAB has IE of 69.4% while 7 ppm of CTAB has *IE* of 88.1% operated at 20 °C. Increase in inhibition efficiency with increase in the concentration is suggestive of the adsorption of the inhibitor onto the mild steel surface. Also, the inhibition efficiency of CTAB in 0.5 M HCl at a relatively low concentration of inhibitor concentration was very low compared with that obtained in 0.1 M HCl solution at the same inhibitor concentration, so, a high inhibitor concentration up to 25 ppm was used. These results indicated that the concentration of HCl plays an important role in the inhibition efficiency.

The effect of temperature change on the corrosion rate was examined and the apparent activation energies (E_a) were calculated from the Arrhenius equation[21]:

$$\log (CR_2/CR_1) = E_a /2.303\ R\ (1/T_1-1/T_2) \qquad (5)$$

Where CR_1 and CR_2 are the corrosion rates at temperature T_1 (303K) and T_2 (313K) respectively, and R is the general gas constant that equals 8.314 J/mol k. The calculated values for E_a are given in TABLE 3. From the data listed in this table, it was found that values of E_a increase with increasing the inhibitor concentration either in 0.1 M HCl or in 0.5 M HCl. Generally, a corrosion inhibitor is a substance that increases the activation energy of the corrosion process and this is clear from the obtained values of E_a in different concentrations of acid solution in the presence of the investigated inhibitor. This means that the energy barrier for the corrosion reaction increases in the presence of the inhibitor, where the corrosion reaction will be further pushed to surface sites that are characterized by higher values of E_a. This indicates that the corrosion of carbon steel occurs at the uncovered part of its surface. The value of E_a for the investigated inhibitors increases according to the inhibitor concentration increase. This order is the same as that of the inhibition efficiency. Additionally, increased E_a in inhibited solutions compared with that of the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface. While, either unchanged or lower values of E_a in the presence of inhibitor suggest chemisorptions process is most predominated[22,23]. The present results revealed that the adsorption is physical adsorption.

CTAB inhibited steel corrosion due to the adsorption of the n-cetyl group on the steel surface. The surface of the steel electrode was positively charged in hydrochloric acid solution at the corrosion potential. The steel corrosion inhibition of CTAB was attributed to the synergistic effect between bromide anions and positive quaternary ammonium ions. The $C_{16}H_{33}N(CH_3)_3^+$ ions may electrostatically adsorb on the steel surface, which is primarily covered with adsorbed bromide ions.

TABLE 3 : Calculated values of activation energy (E_a) for low carbon Steel in 0.1 and 0.5 M HCl in the absence and presence of inhibitor

Concentration of Inhibitor, ppm	**E_a ($KJmol^{-1}$) In 0.1 M HCl**
Blank	11.5
3	75.8
5	126.2
7	137.5
Concentration of Inhibitor, ppm	Ea ($KJmol^{-1}$) In 0.5 M HCl
Blank	29.9
5	127
15	183.8
25	247

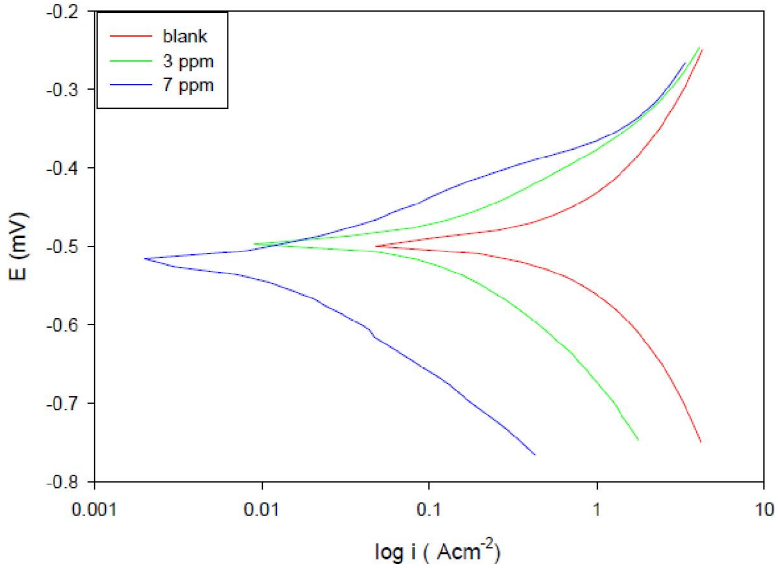

Figure 3 : The potentiodynamic polarization curves of carbon steel in 0.1 M HCl without and with different concentrations of CTAB operated at 25 °C

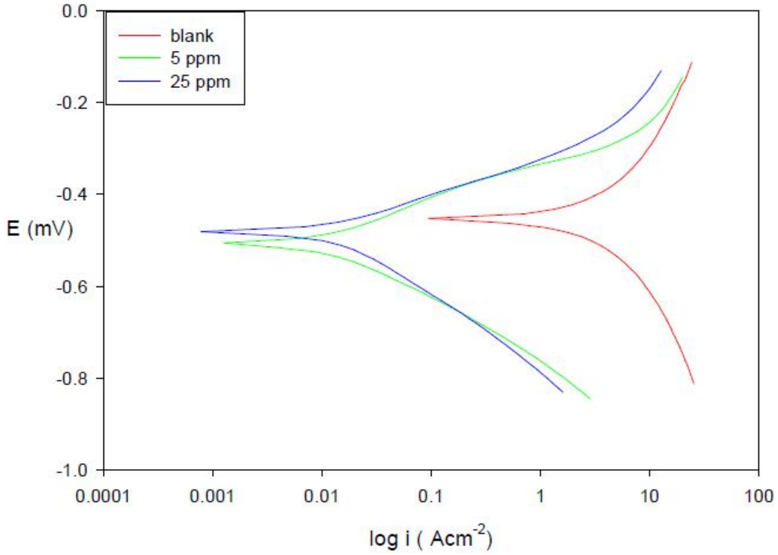

Figure 4 : The potentiodynamic polarization curves of carbon steel in 0.5 M HCl without and with different concentrations of CTAB operated at 25 °C

Polarization measurement

Anodic and cathodic polarization curves were recorded to obtain information about the action of the inhibitor on the partial corrosion processes. Figures 3 and 4 show the polarization curves measured on carbon steel electrodes in each of 0.1and 0.5 M HCl solutions at 20 °C (293 K) in absence and in presence of CTAB inhibitor. The electrochemical parameters, such as the corrosion current density (i_{corr}), the corrosion potential (E_{corr}), anodic (b_a) and cathodic (b_c) Tafel slopes, were obtained by Tafel extrapolation and are reported in TABLE 4. It is observed that the corrosion current density of the anodic and cathodic branch is displaced towards lower values. This displacement is more evident with the increase in concentration of the inhibitor.

It can be seen from the results that I_{corr} values decreases with increasing the CTAB concentration range in 0.1 and 0.5 M HCl solutions. Maximum reduction of I_{corr} for CTAB is obtained at 7 ppm concentration in 0.1 M HCl and 25 ppm concentration in 0.5 M HCl. It clear from data in TABLE 4 that a slight change in the anodic Tafel slope values with increasing the inhibitor concentration, but an obvi-

TABLE 4 : Variation of polarization parameters for low carbon steel in 0.1 M and 0.5 M HCl solutions at 25 C^{o} with different CTAB concentration inhibitor

At 0.1M HCl	Conc$_{inh}$, ppm	Ecorr, mV	icorr, mA cm^{-2}	-bc, mV dec^{-1}	ba, mV dec^{-1}	IE %
	0	-509	1439	226	248	
	3	-506	475	203	242	67.00
	7	-525	133	180	240	90.70
At 0.5M HCl	**0**	**-473**	**4104**	**235**	**257**	
	5	-506	1062	175	244	74.10
	25	-491	249	168	234	93.90

ous decrease in the cathodic Tafel slope is observed with increasing the inhibitor concentration, this means that the inhibitor affects the cathodic reaction and decreases the hydrogen evolution reaction.

Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of carbon steel in 0.1 and 0.5 M HCl solutions in the absence and presence of different concentrations of inhibitor (for each concentration of acid) was investigated by AC impedance spectra technique (electrochemical impedance spectra) (EIS) at 20 °C as shown in Figures 5 & 6 (Nyquist plots) and in Figures 7 & 8 (Bode plots). The impedance (log *Z*/Ω) values derived from Bode plots are also given in TABLES 5 & 6. Using Ivium software, the impedance spectra of the different Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit model. It was found that the equivalent circuit that fit the experimental data consists of one time constant model $R_s(R_pC_{dl})$ for carbon steel electrodes in HCl solutions as a given in Figure 9. It includes the solution resistance R_s and the double layer capacitance C_{dl} which is placed in parallel to the polarization resistance R_p. The obtained Nyquist impedance diagrams in most cases does not show perfect semicircle, generally attributed to the frequency dispersion as a result of roughness and in homogenates of the electrode surface. The data reveal that, each impedance diagram consists of a large capacitive loop with low frequencies dispersion.

The results of simulation of all the measured impedance spectra for the carbon steel at different conditions as illustrated in TABLES 5 &6 reveal that, when mild steel is immersed in 0.1 M HCl aqueous solution containing 7 ppm CTAB, the polarization resistance (R_p) and the double layer capacitance (C_{dl}) (derived from Nyquist plots) are 114 ohm cm^2

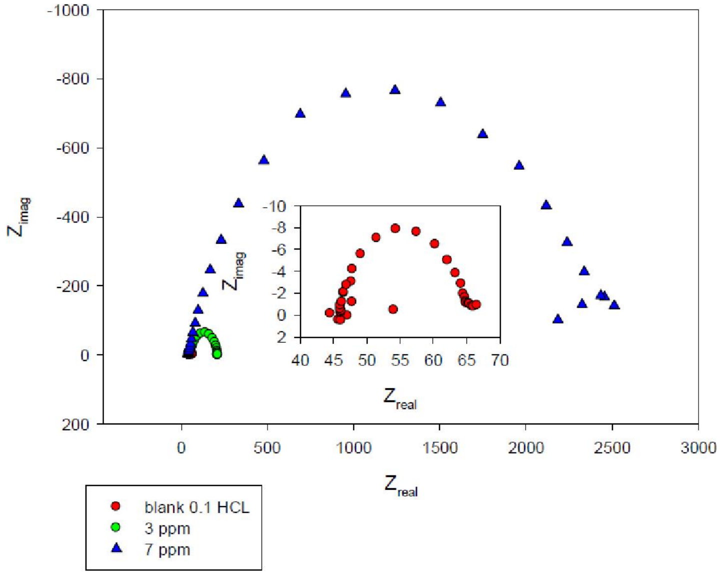

Figure 5 : Nyquist plots for carbon steel in 0.1 M HCl in the absence and presence of different concentrations of CTAB operated at 25 °C

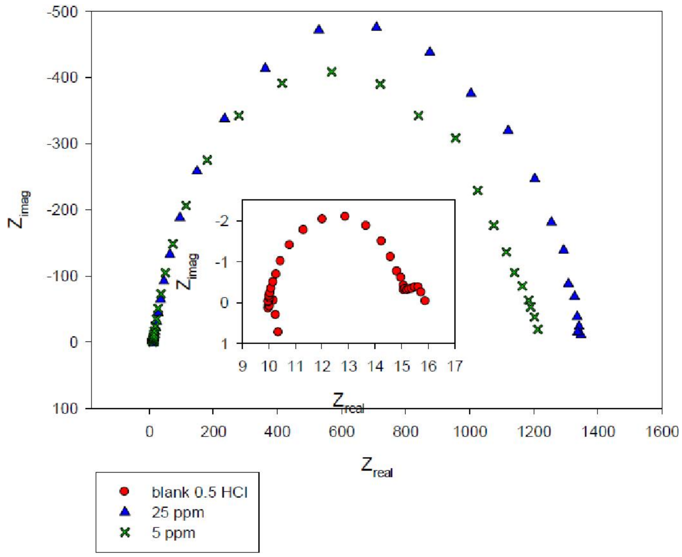

Figure 6 : Nyquist plots for carbon steel in 0.5 M HCl in the absence and presence of different concentrations of CTA operated at 25 °C

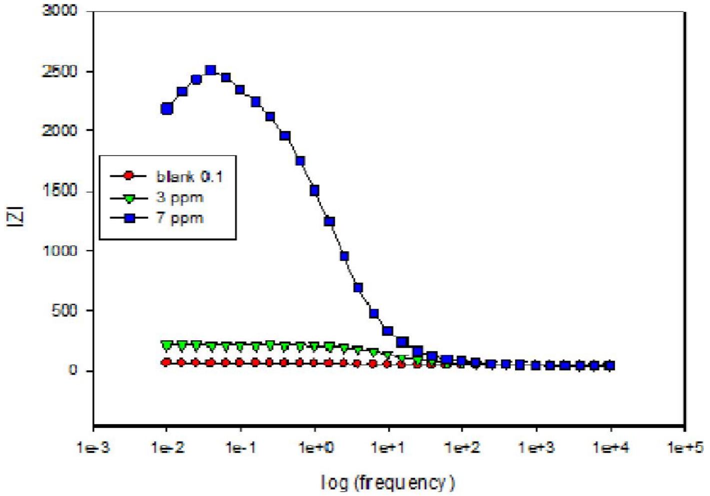

Figure 7 : Bode plots of carbon steel in 0.1 M HCl solutions containing CTAB

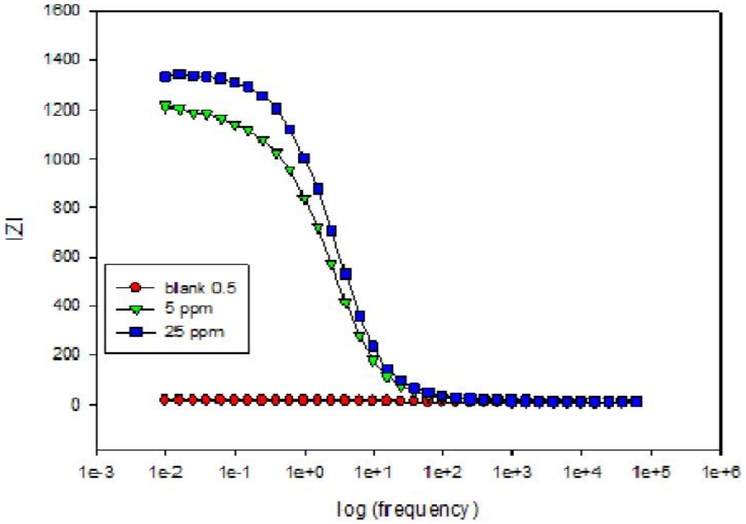

Figure 8 : Bode plots of carbon steel in 0.5 M HCl solutions containing CTAB inhibitor

TABLE 5 : Electrochemical kinetic parameters obtained from EIS technique for the corrosion of carbon steel in 0.1 HCl at CTAB different concentrations operated at 25 °C

Conc., ppm	C_{dI}, µF cm^{-2}	R_s ohm cm^2	R_{ct}, ohm cm^2	Impedance log(Z/Ω)	IE %	n %
Blank	1787	46.9	18	1.25		0.9819
3 ppm	87	53.4	155.8	2.19	88.4	0.9841
7 ppm	44	114	2130	3.32	99.1	0.984

TABLE 6 : Electrochemical kinetic parameters obtained from EIS technique for the corrosion of carbon steel in 0.5 HCl at CTAB different concentrations operated at 25 °C

Conc., ppm	C_{dI}, µF cm^{-2}	R_s ohm cm^2	R_{ct}, ohm cm^2	Impedance log(Z/Ω)	IE %	n %
Blank	6302	10	5.1	0.70		0.990
5 ppm	63	40.3	1078	3.03	99.5	0.984
25 ppm	47	44.8	1227	3.08	99.6	0.984

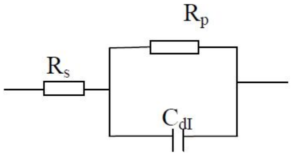

Figure 9 : The equivalent circuit model used to fit the experimental results

and 44 µF cm^{-2}, respectively. The impedance log (Z/Ω), value derived from bode plots is 3.3. While, when mild steel is immersed in 0.5 M HCl aqueous solution containing 25 ppm of CTAB, the R_p is 44.8 ohm cm^2 and the double layer capacitance (C_{dI}) is 47 µF cm^{-2} and the impedance log (Z/Ω) value is 3.

It can be seen that as carbon steel immersed in aqueous solution of 0.1 M HCl containing 7 ppm of inhibitor the R_s increases from 46.9 to 114 ohm cm^2, the C_{dI} value decreases from 1787 to 44 µF cm^{-2} and the impedance value increases from 1.25 to 3.3. Moreover, it can be noticed that the same trend was obtained when carbon steel immersed in 0.5 M HCl aqueous solution containing 25 ppm of inhibitor, the R_p increases from 10 to 44.8 ohm cm^2, the C_{dI} value decreases from 6302 to 47 µF cm^{-2} and the impedance value increases from 0.7 to 3. This indicates that the film formed on the metal surface due to the presence of inhibitor which lead to the decrease in local dielectric constant and increase in thickness of the electrical double layer, suggests that CTAB acts via adsorption at the metal / solution interface[24-26].

Adsorption isotherms

Basic information on the interaction between the inhibitors molecules and the carbon steel can be provided by the adsorption isotherm. Two main types of interaction can describe the adsorption of the organic compound: physical adsorption and chemical adsorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and the nature of the metal. The surface coverage (θ) of the metal surface by the adsorbed inhibitor was evaluated from weight loss measurement using the following relation:

$$\theta = W_0 – W / W_0 \qquad (6)$$

The Langmuir isotherm[27] was found to provide the best description of the adsorption behavior.

$$C/\theta = 1/K + C \qquad (7)$$

Where C is the concentration of inhibitor and K is the adsorptive equilibrium constant. Plotting of C/ô Vs C for carbon steel in 0.1 and 0.5 M HCl solutions and in presence of different concentration of inhibitor yields a straight line as shown in Figures 10. In both cases the linear regression coefficients (R^2) are almost equal to 1 and the slopes are very close to 1, indicating that the adsorption of CTAB obeys the Langmuir isotherm and there is a negligible interaction between the adsorbed molecules. K_{ads} values can be calculated from the intercepts of the straight lines on the C/θ-axis, the K_{ads} is related to the standard free energy of adsorption, $\Delta G°_{ads}$ with the following equation:

$$\Delta G°_{ads} = -RT \text{ Ln } (C_{H2O} . K_{ads}) \qquad (8)$$

In equation (7), we use C_{H2O} which is the molar concentration of water in solution in g/L and K_{ads} is the equilibrium constant of the inhibitor adsorption process, in L/g, the unit of $\Delta G°_{ads}$ depends only on the factor RT (kJ.mol^{-1}). Thermodynamic parameters

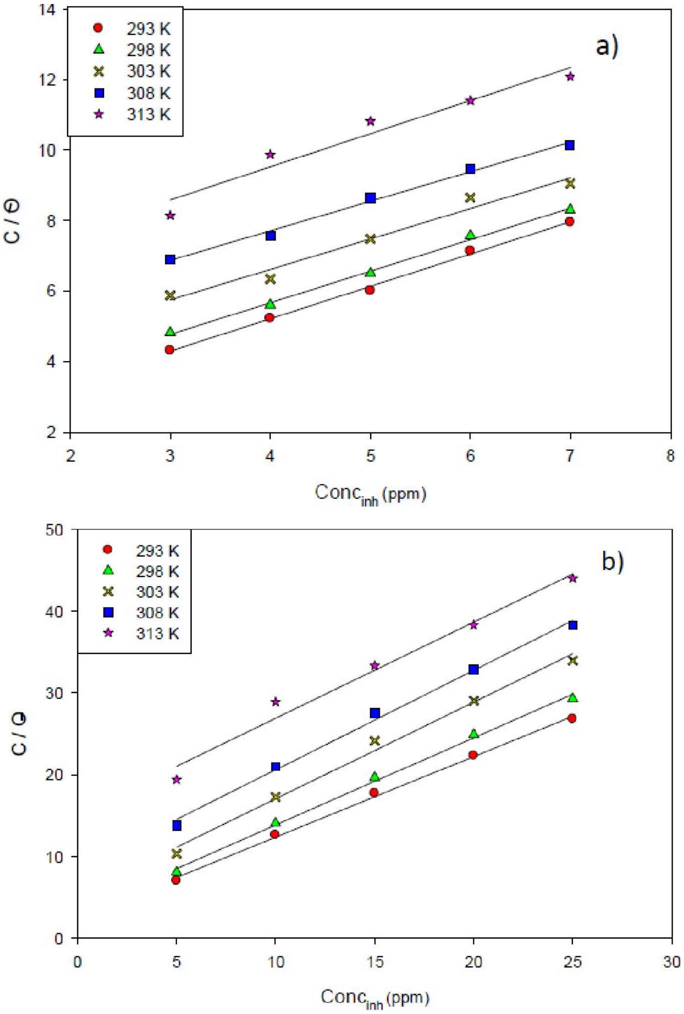

Figure 10 : Langmuir adsorption isotherm of CTAB on carbon steel surface in a) 0.1 M HCl and b) 0.5 M HCl at different temperature

for adsorption process obtained from Langmuir's adsorption isotherm for the studied inhibitor are given in TABLES 7and 8.

The negative values of $\Delta G°_{ads}$ (TABLE 7 and 8) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface[28]. It is generally accepted that for the values of $\Delta G°_{ads}$ up to -20 kJ mol^{-1}, the types of adsorption were regarded as physisorption, the inhibition acts due to the electrostatic interaction between the charged particles and the metal (Wander Val force), while the values around -40 kJ mol^{-1}, were seen as chemisorption, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface in a covalent bond[29, 30]. The $\Delta G°_{ads}$ values obtained in this study range from -31.4 to -32.6 kJ mol^{-1}for 0.1M HCl and from -30.6 to -31.5 kJ mol^{-1}for 0.5M HCl. It suggested that the adsorption mechanism of the CTAB on carbon steel in HCl solution was typical of the two processes physisorption and chemisorptions. The heat of adsorption ΔH° is obtained from the Van't Hoff's equation[31]:

$$\mathbf{Ln}\ K_{ads} = -\frac{\Delta H}{RT} + \text{constant} \qquad (9)$$

When ln K_{ads} vs. (1/T) is plotted, the values of ΔH are obtained from the slope. The negative sign of $\Delta H°_{ads}$ in 0.1 or 0.5 M HCl solution indicates that the adsorption of inhibitor molecule is an exothermic process. Generally, an exothermic adsorption process signifies either physic- or chemisorption while endothermic process is attributable unequivocally to chemisorption[32]. Moreover, the entropy (ΔS) is obtained for a range of temperatures with

TABLE 7 : Thermodynamic parameters for the adsorption of CTAB on low carbon steel surface in 0.1M HC1

T(K)	K_{ads}(L/g)	$\Delta G°_{ads}$ (kJ mol^{-1})	$\Delta H°_{ads}$(kJ mol^{-1})	$\Delta S°_{ads}$(KJ mol^{-1} K^{-1})
293	0.64766	-32.6	-51.4	-0.0641
298	0.4781	-32.4		-0.0637
303	0.31665	-31.9		-0.0643
308	0.2289	-31.6		-0.0642
313	0.17343	-31.4		-0.0639

TABLE 8 : Thermodynamic parameters for the adsorption of CTAB on low carbon steel surface in 0.5M HCl

T(K)	K_{ads}(L/g)	$\Delta G°_{ads}$ (kJ mol^{-1})	$\Delta H°_{ads}$(kJ mol^{-1})	$\Delta S°_{ads}$(KJ mol^{-1} K^{-1})
293	0.4053	-31.5	-70.1	-0.1317
298	0.3148	-31.4		-0.1298
303	0.1916	-30.6		-0.1303
308	0.1185	-29.9		-0.1305
313	0.06585	-28.9		-0.1316

the following equation.

$$\Delta G° = \Delta H°_{ads} - T\,\Delta S°_{ads} \qquad (10)$$

The negative values of ΔS_{ads} may be explained in the following way: before the adsorption of inhibitors onto carbon steel surface, inhibitor molecules freely move in the bulk solution, but with the progress in the adsorption process, inhibitor molecules were orderly adsorbed onto carbon steel surface, and hence, the entropy decrease.

CONCLUSION

The following main conclusions are drawn from the present study:

1. Corrosion of low carbon steel in 0.1M and 0.5M HCl is efficiently inhibited by CTAB.
2. The inhibition efficiency of CTAB increases with increase in inhibitor concentration.
3. The inhibitor showed maximum inhibition efficiency at 7 ppm concentration in 0.1 M HCl and at 25 ppm in 0.5 M HCl.
4. Langmuir adsorption isotherm and impedance studies showed that CTAB inhibits the corrosion through adsorption mechanism.
5. Potentiodynamic polarization curves showed that CTAB acted as a cathodic inhibition.
6. CTAB inhibited steel corrosion due to the adsorption of the n-cetyl group on the steel surface. The surface of the steel electrode was positively charged in hydrochloric acid solution at the corrosion potential. The steel corrosion inhibition of CTAB was attributed to the synergistic effect between bromide anions and positive quaternary ammonium ions. The $C_{16}H_{33}N(CH_3)_3^+$ ions may electrostatically adsorb on the steel surface, which is primarily covered with adsorbed bromide ions.

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REFERENCES

[1] R.P.Bothi, R.A.Abdul, O.Hasnah, A.Khalijah; Inhibitory effect of kopsia singapurensis extract on the corrosion behavior of mild steel in acid media, Acta Phys.Chim.Sin., **26**, 2171- 2176 **(2010)**.

[2] M.Hosseini, M.Ehteshamzadeh, T.Shahrabi; Protection of mild steel in 0.5 M H_2SO_4 solution, Electrochim.Acta, **52**, 3680- 3685 **(2007)**.

[3] H.Tavakoli, T.Shahrabi, M.Hosseini; Synergistic effect on corrosion inhibition of copper by sodium dodecylbenzenesulphonate(SDBS) and2-mercaptobenzoxazole, Mater.Chem.Phys., **109**, 281-286 **(2008)**.

[4] R.A.Prabhu, T.V.Venkatesha, A.V.Shanbhag, G.M.Kulkarni, R.G.Kalkhambkar; Inhibition effects of some Schiff's bases on the corrosion of mild steel

in hydrochloric acid solution, Corros.Sci., **50**, 3356-3362 **(2008)**.

[5] S.K.Shukla, M.A.Quraishi; Ceftriaxone: A novel corrosion inhibitor for mild steel in hydrochloric acid, *J.Appl.Electrochem*., **39**, 1517-1523 **(2009)**.

[6] S.K.Shukla, M.A.Quraishi; 4-Substituted anilinomethylpropionate: New and efficient corrosion inhibitors for mild steel in hydrochloric acid solution, *Corros.Sci*., **51**, 1990-1997 **(2009)**.

[7] P.Kern, D.Landolt, Y.Abboud; Adsorption of an organic corrosion inhibitor on iron and gold studied with a rotating EQCM, J.Electrochem.Soc., **148**, B228-B235 **(2001)**.

[8] A.J.Aldykewicz, H.S.Isaacs, A.J.Davenport; The Investigation of Cerium as a Cathodic Inhibitor for Aluminum Copper Alloys, J.Electrochem.Soc., **142**, 3342-3350 **(1995)**.

[9] B.Muller; React.Funct.Polym., Polymeric corrosion inhibitors for aluminium pigment, **39**, 165-177 **(1999)**.

[10] R.Hasanov, M.Sadikoglu, S.Bilgic; Electrochemical and quantum chemical studies of some Schiff bases on the corrosion of steel in H_2SO_4 solution, *Appl.Surf.Sci.,* **253**, 3913-3921 **(2007)**.

[11] A.Chetouani, B.Hammouti, T.Benhadda, M.Daoudi; Inhibitive action of bipyrazolic type organic compounds towards corrosion of pure iron in acidic media, *Appl.Surf.Sci.,* **249**, 375-385 **(2005)**.

[12] M.Bouklah, B.Hammouti, M.Lagrenee, F.Bentiss; Thermodynamic properties of 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole as a corrosion inhibitor for mild steel in normal sulfuric acid medium, Corros.Sci., **48**, 2831-2842 **(2006)**.

[13] M.Benabdellah, R.Touzani, A.Aouniti, A.Dafali, S.El-Kadiri, B.Hammouti, M.Benkaddour; Inhibitive action of some bipyrazolic compounds on the corrosion of steel in 1 M HCl: Part I: Electrochemical study, Mater.Chem.Phys., **105**, 373-379 **(2007)**.

[14] A.Yildirim, M.Cetin; Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors, *Corros.Sci.,* **50**, 155-165 **(2008)**.

[15] K.F.Khaled, M.M.Al-Qahtani; The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution: Chemical, electrochemical and theoretical studies, *Mater.Chem.Phys.,* **113**, 150-158 **(2009)**.

[16] H.Ma, T.Song, H.sun, X.Li; Experimental and theoretical elucidation on the inhibition mechanism of 1-methyl-5-mercapto-1,2,3,4-tetrazole self-assembled films on corrosion of iron in 0.5 M H_2SO_4 Solutions, *Thin solid films,* **516**, 1020-1024 **(2008)**.

[17] H.Ju, Z.P.Kai, Y.Li; Aminic nitrogen-bearing polydentate Schiff base compounds as corrosion inhibitors for iron in acidic media: A quantum chemical calculation, *Corros.Sci.,* **50**, 865-871 **(2008)**.

[18] G.Trabanelli; in: F.Mansfeld (Edition), Corrosion Mechanisms, Marcel Dekker, New York, 119 **(1987)**.

[19] Z.Abdel Hamid, T.Y.Soror, H.A.El-Dahan, A.M.A.Omar; New Cationic Surfactant as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution, Anti-corros.Meth.Mater., **45(5)**, 306–311 **(1998)**.

[20] H.Luo, Y.C.Guan, K.N.Han; Corrosion Inhibition of a Mild Steel by Aniline and Alkylamines in Acidic Solutions, Corros., **54**, 721-731 **(1998)**.

[21] M.Bhardwaj, R.Balasubramaniam; Uncoupled non-linear equations method for determining kinetic parameters in case of hydrogen evolution reaction following Volmer–Heyrovsky–Tafel mechanism and Volmer–Heyrovsky mechanism, *International journal of Hydrogen Energy,* **33**, 2178-2188 **(2008)**.

[22] U.F.Ekanem, S.A.Umoren, I.I.Udousoro, A.P.Udoh; Inhibition of mild steel corrosion in HCl using pineapple leaves (Ananas comosus L.) extract, Journal of Mater.Sci., **45**, 5558 -5566 **(2010)**.

[23] G.Moretti, G.Quartarone, A.Tassan, A.Zingoles; 5-Amino- and 5-chloro-indole as mild steel corrosion inhibitors in 1 N sulphuric acid, *Electrochem.Acta*, **41**, 1971-1980 **(1996)**.

[24] J.Sathiyabama, S.Rajendran, J.Arokia selvi; Bull.Electrochemistry, **22**, 363 **(2006)**.

[25] M.A.Quraishi, J.Rawat; Influence of iodide ions on inhibitive performance of tetraphenyl-dithia-octaaza-cyclotetradeca-hexaene (PTAT) during pickling of mild steel in hot sulfuric acid, *Mater.Chem.Phys.,* **70**, 95-99 **(2001)**.

[26] M.A.Amin, S.S.A.El-Rehim, E.E.F.El-Sherbini, R.S.Bayoumy; The inhibition of low carbon steel corrosion in hydrochloric acid solutions by succinic acid: Part I.Weight loss, polarization, EIS, PZC, EDX and SEM studies, *Electrochimica.Acta,* **52**, 3588-3600 **(2007)**.

[27] R.Agrawal, T.K.G.Namboodhiri; The inhibition of sulphuric acid corrosion of 410 stainless steel by thioureas, Corros.Sci., **30**, 37-52 **(1990)**.

[28] A.Popova, E.Sokolova, S.Raicheva, M.Chritov; AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives, Corros.Sci., **45**, 33-58

(2003).

[29] Z.Szlarska-Smialowska, J. Mankovwski; Crevice corrosion of stainless steels in sodium chloride solution, Corros. Sci., **18**, 953-960 **(1978)**.

[30] A.Yurt, S.Ulutas, H.Dal; Applied Surface Science, **253(2)**, 919 **(2006)**.

[31] T.P.Zhao, G.N.Mu; The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid, Corros.Sci., **41**, 1937-1944 **(1999)**.

[32] B.Donnely, T.C.Downie, R.Grzeskowiak, H.R.Hamburg, D.Short; The effect of electronic delocalization in organic groups R in substituted thiocarbamoyl R-CS-NH_2 and related compounds on inhibition efficiency, Corros.Sci., **18**, 109-118 **(1978)**.