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## The theobromine (chocolate) as green inhibitor of mild steel corrosion in hydrochloric acid: Electrochemical and theoretical quantum studies

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### ABSTRACT

The inhibitive action of Theobromine on corrosion of mild steel in 1M HCl solution has been studied using weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. It was found that the inhibition efficiency of Theobromine inhibitor increases with increase in concentration of inhibitor and decreases with increase in temperature. The inhibitor show corrosion inhibition efficiency of 90% at 1g/l and 308 K. Polarization data suggested that the Theobromine inhibitor used as mixed type inhibitor. Impedance measurements indicating that the corrosion reaction is controlled by charge transfer process. The adsorption of Theobromine on the metal surface was found to obey Langmuir adsorption isotherm. The Density Functional Theory (DFT) was employed for quantum chemical calculations to correlate the experimental findings.

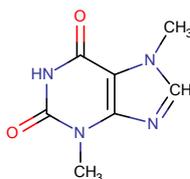
**Key words:** Theobromine, Mild steel, EIS, Corrosion, 1M HCl, DFT.

### INTRODUCTION

Using inhibitors is one of the most practical methods for protecting metals against corrosion, especially in acidic media [1]. Among numerous inhibitors, N-heterocyclic compounds are considered to be the most effective corrosion inhibitors [2]. Up to now, various N heterocyclic compounds are reported as good corrosion inhibitors for mild steel in acidic media [3, 4]

The interaction between the metal surface and hetero atoms such as nitrogen, oxygen and sulfur plays an important role in inhibition process. These atoms possess free electron pairs which facilitate their adsorption on the metal surface where they can displace water and form protective film on the surface of the metal [5, 6]. Protection of the equipments and vessels against corrosion is a major concern of the maintenance and design engineers. The use of chemical inhibitors is one of the most effective measures for protecting the metal surfaces against corrosion in such highly acidic media [7].

The objectives of this work were to study the inhibition performance of Theobromine (Scheme 1), using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. For further confirmation several isotherms were tested for their relevance to describe the adsorption behavior of the compound studied. The correlation between the inhibition efficiency of used inhibitors and quantum chemical parameters was also studied.



Scheme 1: Chemical structure of the investigated Theobromine inhibitor

## MATERIALS AND METHODS

### 2.1. Solutions and samples preparation

Corrosion experiments were performed on mild steel specimens with weight percentage composition as follows: 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S and the remainder Fe. Specimens were wet-ground using emery paper from grade N°400 to N°1200; rinsed with distilled water, degreased with acetone and dried with warm air before use.

### 2.2. Weight loss, polarization and EIS measurements

Weight loss measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (1.5 cm x 1.5 cm 0.05 cm). The immersion time for the weight loss was 6 h at 308 K. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Weight loss allowed us to calculate the mean corrosion rate as expressed in  $\text{mg cm}^{-2} \text{h}^{-1}$ .

Electrochemical measurements were carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) in the form of disc cut from mild steel has a geometric area of  $1 \text{ cm}^2$  and is embedded in polytetrafluoroethylene polytetrafluoroethylene. A saturated calomel electrode (SCE) and a disc platinum electrode were used, respectively, as reference and auxiliary electrodes. The temperature was thermostatically controlled at  $308 \pm 1 \text{ K}$ .

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltmaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of  $0.5 \text{ mV/s}$ . Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from  $-800 \text{ mV}$  to  $-200 \text{ mV}$  at 308 K. The solution test is there after de-aerated by bubbling nitrogen. The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage ( $10 \text{ mV}$ ) peak to peak, at frequencies between  $100 \text{ kHz}$  and  $10 \text{ mHz}$  are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30min of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

### 2.3. Quantum chemistry calculation

The quantum calculations were performed using the GAUSSIAN 09 program [8]. The geometry of the studied compound was evaluated using the Density Functional Theory (DFT) level of the three-parameter compound functional of Becke (B3LYP) [9]. The 6-31 G(d,p) basis set was used for all atoms. The geometry geometry structure was optimised under no constraints. We have also examined HOMO and LUMO levels; the energy gap was evaluated as the difference between the HOMO and LUMO due to the MO energies. And the Density Functional Theory (DFT) approach was performed on Theobromine to determine the relationship between inhibition efficiency and their molecular structure.

## RESULTS AND DISCUSSION

### 3.1. Weight loss measurements

#### 3.1.1. Effect of inhibitor concentration

Corrosion of mild steel in 1 M HCl containing different concentrations (1- 0.125g) of Theobromine was studied by weight loss measurements, that is, measuring the mass of metal turned into corrosion products per unit area of surface per unit of time. The immersion time was optimized and the optimized 6 h immersion time was used for all the weight loss measurements. Coupons were removed from the electrolyte after 6 h, washed thoroughly with

distilled water. Triplicate experiments were conducted for each concentration of the inhibitors to ensure reproducibility and the corrosion rate ( $w$ ), inhibition efficiency ( $E\%$ ) and surface coverage ( $\theta$ ) were determined by following equations [10]:

$$E(\%) = \left(1 - \frac{W'_{CORR}}{W_{CORR}}\right) \cdot 100 \quad (1)$$

Where  $W_{corr}$  and  $W'_{corr}$  are the corrosion rates of mild steel due to the dissolution in 1 M HCl in uninhibited and inhibited solutions, respectively.

**Table 1. Corrosion parameters obtained from weight loss measurements for mild steel in 1 M HCl containing various concentrations of Theobromine at 308 K**

Inhibitor	Concentration (g/l)	$W_{corr}$ ( $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ )	$E_w$ (%)	$\theta$
Theobromine	HCl 1M	0.91	--	--
	1	0.09	90	0.90
	0.5	0.13	86	0.86
	0.25	0.17	81	0.81
	0.125	0.26	70	0.70

The analysis of these results (Table 1) shows clearly that the corrosion rate decreases ( $W$  ( $\text{mg/h cm}^2$ )) while the inhibition efficiency ( $E_w\%$ ) increases with increasing inhibitor concentration reaching a maximum value of 90% at a concentration of 1g/L. This behavior can be attributed to the increase of the surface covered  $\theta$  ( $E_w\%/100$ ), and that due to the adsorption of natural compound (Theobromine) on the surface of the mild steel, as the inhibitor concentration increases. We can conclude that Theobromine is a good corrosion inhibitor for steel in 1 M HCl solution.

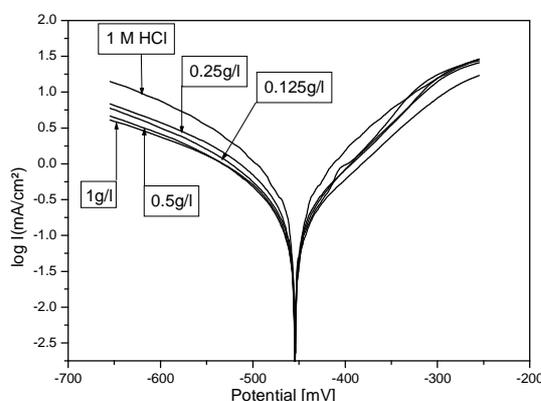
### 3.1.2. Potentiodynamic (Tafel) polarization measurements

The effect of different concentrations of Theobromine inhibitor on the potentiodynamic polarization behavior of mild steel in 1 M HCl solution at 308K was shown in Figure 1. Corrosion parameters, such as corrosion potential ( $E_{corr}$ ), cathodic Tafel slopes ( $\beta_c$ ) and corrosion current density ( $I_{corr}$ ) obtained by extrapolation of the Tafel lines and the inhibition efficiency values  $E_p\%$  are listed in Table 2. From the polarization curves, it was noted that both the rate of cathodic and anodic reactions are reduced as the concentrations of inhibitor increased by reducing the current densities on both sides. This result suggests that the addition of the inhibitor reduce anodic dissolution and also retards the hydrogen evolution reaction [11]. The electrochemical processes on the metal surface are related to the adsorption of the inhibitor and the adsorption is known to depend on the chemical structure of the inhibitor.

The inhibition efficiency ( $E\%$ ) was calculated according to equations (2) and is depicted in Table 2.

$$E_p\% = \frac{I_{corr(0)} - I_{corr(inh)}}{I_{corr(0)}} \times 100 \quad (2)$$

where  $I_{corr(0)}$  and  $I_{corr}$  are current density in absence and presence of Theobromine, respectively.



**Figure 1. Potentiodynamic polarization curves of mild steel in 1M HCl in the presence of different concentrations of Theobromine**

The results as presented in Table 2 and Figure 1 showed that, there is a slight difference in the values of  $E_{\text{corr}}$  between the inhibitor containing systems and the blank system. However, it is important to state that the  $E_{\text{corr}}$  values for the inhibitor containing systems shift essentially towards the cathodic and anodic regions relative to that of the blank as shown in Figure 1. The maximum shift in  $E_{\text{corr}}$  value relative to the  $E_{\text{corr}}$  of the blank is 10 mV vs, SCE. Since an inhibitor can only be regarded as anodic or cathodic type when the displacement in  $E_{\text{corr}}$  is greater than 85 mV [12-14], thus, this Theobromine can be arranged as mixed-type inhibitor.

**Table 2. Electrochemical parameters of mild steel in 1M HCl solution without and with Theobromine at different concentrations**

Inhibitor	Concentration (g/l)	$E_{\text{corr}}$ (mV/SCE)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$\beta\text{c}$	$E_p$ (%)
HCl 1M	--	-459	1386	-294	--
Theobromine	1	-454	134	-294	90
	0.5	-451	178	-287	87
	0.25	-450	181	-289	87
	0.125	-449	351	-295	75

Also the data in Table 2 indicates that the Theobromine have no effect on the metal dissolution mechanism since the slopes of the cathodic Tafel lines ( $\beta\text{c}$ ) are approximately constant and independent on the inhibitor concentration. Evidently, the gradual increase in the inhibitor concentration moves the corrosion current densities towards lower values. The  $I_{\text{corr}}$  values for the Theobromine inhibitor at 1g/l concentration were found to be  $134 \mu\text{A}/\text{cm}^2$  (Table 2) which is significantly lower than  $1386 \mu\text{A}/\text{cm}^2$  found for the mild steel in free HCl. In this order, the decrease of current density in the presence of the inhibitor reveal that the corrosion reaction proceeds much slower in the inhibited medium than the uninhibited medium. Moreover, the gradual increase of the inhibitor concentrations decreases the corrosion current densities. Also the data in Table 2 indicates that the increase of inhibitor concentrations increases the surface coverage values which consequently decrease the corrosion current densities. The results obtained from the polarization measurements are in good agreement with those obtained from the gravimetric method.

### 3.1.3. Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of mild steel in 1 M HCl solution with and without Theobromine inhibitor is also investigated by the electrochemical impedance spectroscopy (EIS) at 308K after 30 min of immersion. The charge-transfer resistance ( $R_t$ ) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru [15]. The double-layer capacitance ( $C_{\text{dl}}$ ) and the frequency at which the imaginary component of the impedance is maximal ( $-Z_{\text{max}}$ ) are found as represented in the following equation:

$$f_{\text{max}} = 1/2\pi C_{\text{dl}}R_t \quad (3)$$

where  $f_{\text{max}}$  is the frequency at which the imaginary component of the impedance ( $Z_{\text{im}}$ ) is maximum and  $R_t$  is the diameter of the loop.

Impedance diagrams are obtained for frequency range 100 KHz–10 mHz at the open circuit potential for steel in 1 M HCl in the presence and absence of Theobromine. Nyquist plots for mild steel in 1 M HCl at various concentrations of Theobromine is presented in Figure 2. Table 3 gives values of charge transfer resistance  $R_t$  double-layer capacitance  $C_{\text{dl}}$  and inhibition efficiency  $E_{\text{Rt}}$ , the inhibition efficiency got from the charge-transfer resistance is calculated by the following relation:

$$E_{\text{Rt}} \% = \frac{R_{t(\text{inh})} - R_{t(0)}}{R_{t(\text{inh})}} \times 100 \quad (4)$$

where  $R_{t(0)}$  and  $R_{t(\text{inh})}$  are the charge transfer resistance values in the absence and presence of inhibitor, respectively

Generally, Figure 2 showed that the impedance spectra exhibit one single depressed semicircle, and the diameters of semicircle increases with the inhibitor concentration. The single semicircle can be attributed to the charge transfer that takes place at electrode/solution interface, and the transfer process controls the corrosion reaction of steel and the presence of inhibitor does not change the mechanism of dissolution of steel[16]. It is also clear that these impedance diagrams consists of one large capacitive loop and they are not perfect semicircles and this difference has been attributed to frequency dispersion[17] and the heterogeneity of the metal surface[18].

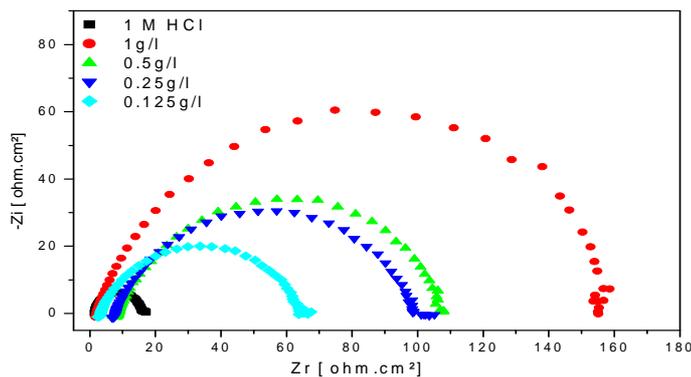


Figure 2. Nyquist plots for mild steel in 1 M HCl containing different concentrations of Theobromine

Table 3. AC impedance data of mild steel in 1.0 M HCl acid solution containing different concentrations of Theobromine at 308K

Inhibitor	Concentration (g/l)	R <sub>t</sub> (Ω.cm <sup>2</sup> )	C <sub>dl</sub> (μf/cm <sup>2</sup> )	E <sub>Rt</sub> (%)
HCl 1M	--	14.7	200	--
Theobromine	1	155	60	90
	0.5	99	64	85
	0.25	91	69	84
	0.125	61	82	75

From the electrochemical polarization data (Table 3), it is clear that the R<sub>t</sub> values increase with inhibitor concentration and consequently the inhibition efficiency increases to 90% at 1 g/L. In fact, the presence of Theobromine is accompanied by the increase of the value of R<sub>t</sub> in acidic solution confirming a charge-transfer process mainly controlling the corrosion of mil steel. Values of double-layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of C<sub>dl</sub> follows the order similar to that obtained for I<sub>corr</sub> in this study. The decrease in C<sub>dl</sub> is due to the adsorption of the inhibitor on the mild steel surface leading to the formation of film or complex from acidic solution [19].

We also note the increase of the value of R<sub>t</sub> with the inhibitor concentration leading to an increase in the corrosion inhibition efficiency. A good agreement is observed between weight loss and electrochemical results.

### 3.2. Effect of temperature

The effect of temperature on the corrosion behavior of mild steel in 1 M HCl containing inhibitor at a concentration 1 g/l is studied in the temperature range 313–343 K using weight loss measurements at 1 h. The data of corrosion rates and corresponding efficiency collected are presented in Table 4.

Table 4 Gravimetric results of steel corrosion in 1 M HCl (1 h immersion) without and with 1 g/l Theobromine at different temperatures

Temperature (K)	W <sub>corr</sub> (mg.cm <sup>-2</sup> .h <sup>-1</sup> )		θ	E <sub>w</sub> (%)
	1M HCl	1M HCl + Theobromine		
313	1.51	0.18	0.88	88
323	3.21	0.61	0.80	80
333	6.53	1.58	0.76	76
343	10.12	4.20	0.58	58

Examination of Table 4 revealed that the corrosion rate increases both in the uninhibited and in the inhibited acid solution with the rise of temperature. The presence of inhibitor leads to decrease of the corrosion rate. E% depends upon the temperature and increases with temperature. The increase in E% indicates that the inhibitory effect of Theobromine is reinforced at elevated temperature.

In acidic solution, the corrosion rate is related to temperature by Arrhenius equation:

$$W_{corr} = k \cdot \exp(-E_a/RT) \quad (5)$$

where k is the corrosion rate constant, E is the activation energy, T is the absolute temperature and R is the universal gas constant.

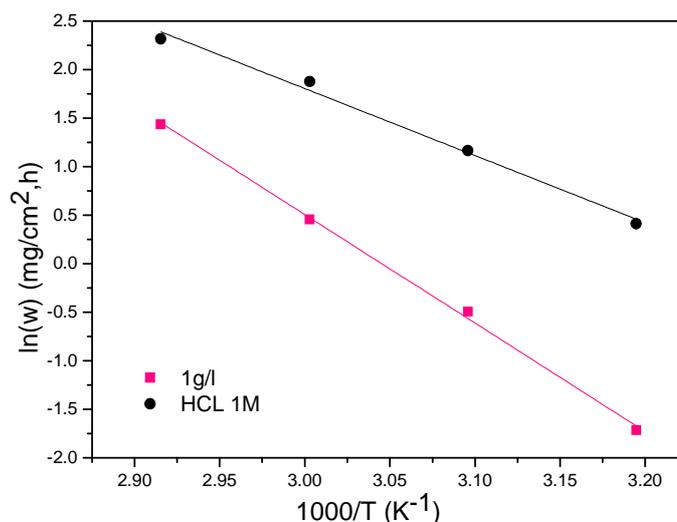


Figure 3. Arrhenius plots of mild steel in 1M HCl with and without 1g/l of Theobromine

The apparent activation energy was determined from the slopes of  $\ln W_{\text{corr}}$  vs  $1/T$  graph depicted in Figure 3. The calculated values of activation energies from the slopes are 92.82 and 57.39 kJ/mol for free acid and with the addition of Theobromine, respectively. We remark that the activation energy change slightly in the presence of inhibitor. Furthermore, the increase of E% is explained by Ammar and El Khorafi [20] as chemisorption of inhibitor molecules on the steel surface. The lower value of  $E_a$  of the corrosion process in an inhibitor's presence when compared to that in its absence is attributed to its chemisorption[21].

### 3.3. Adsorption isotherm

The surface coverage values  $\theta$  were tested graphically for fitting a suitable adsorption isotherm. The plot of  $C_{\text{inh}}/\theta$  versus  $C_{\text{inh}}$  yields a straight line, proving that the adsorption of the inhibitor from HCl solution on the steel surface. This shows that Langmuir isotherm [22] is accurate in all cases (Figure 4):

$$\frac{C}{\theta} = \frac{1}{k} + C \quad (6)$$

With

$$K = \frac{1}{55.55} \exp\left(-\frac{\Delta G_{\text{ads}}^0}{RT}\right) \quad (7)$$

Where  $C$  is the concentration of inhibitor,  $K$  is the adsorptive equilibrium constant,  $\theta$  is the surface coverage and the standard adsorption free energy ( $\Delta G_{\text{ads}}^0$ ).

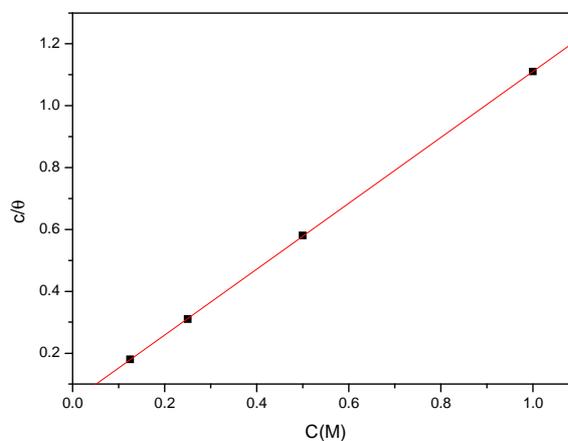


Figure 4. Langmuir adsorption of Theobromine on the mild steel surface in 1 M HCl solution

The  $\Delta G_{\text{ads}}$  values were calculated as  $-42.13 \text{ kJ mol}^{-1}$  for Theobromine. The large negative values indicate the strong interactions between the inhibitor molecules and the metal surface [23]. It is well known that the values of  $\Delta G_{\text{ads}}$  of the order of  $-20 \text{ kJ mol}^{-1}$  or lower indicate a physisorption; those of order of  $-40 \text{ kJ mol}^{-1}$  or higher is related to the chemical adsorption; in other words, charge sharing or transfer between inhibitor molecules and metal to form a coordinate covalent bond (chemisorption) [24]. On the other hand, the adsorption phenomenon of an organic molecule is not considered only as a purely physical or chemical adsorption phenomenon [25]. In this work, the  $\Delta G_{\text{ads}}$  value for Theobromine is closer to  $-40 \text{ kJ mol}^{-1}$ , which indicate the contribution of physical adsorption. Therefore, it is concluded that, the adsorption of Theobromine inhibitor on the mild steel surface is a mixed type of chemical and physical adsorptions with predominantly the first one [26].

### 3.4. Molecular modelling studies

Molecular modelling study was carried out to determine the electron rich groups /atoms in a molecule as well as calculation of the highest molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) will give further insights on the possibility of electron transfer between the inhibitor and metal. The corresponding Frontier molecular orbitals (HOMO and LUMO) are shown in Figure 6.

Figure 7, shows the molecular orbitals of iron ( $\text{Fe}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) while the energy levels viz.,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and  $\Delta E$  calculated are depicted in Table 5, An ideal corrosion inhibitor has a greater tendency to donate electrons, receive electrons or bind strongly to the metal surface [27]. The literature shows that  $E_{\text{HOMO}}$  is often associated with the electron donating ability of the molecule and the (%) increases with increase in the values of  $E_{\text{HOMO}}$  [28].

All quantum chemical parameters were derived from the electronic data of the corresponding optimized structures. The frontier molecular orbital (FMO) energies ( $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ ) are significant parameters for the prediction of the reactivity of a chemical species. The  $E_{\text{HOMO}}$  is often associated with the electron donating ability of a molecule. High  $E_{\text{HOMO}}$  values indicate that the molecule has a high tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. The lower value of  $E_{\text{LUMO}}$  for a molecule suggests that the molecule can readily accept electrons from the donor molecules [29].

The optimized structures, HOMO and LUMO electron density surfaces of the studied molecule is shown in Figure 6. For all the Theobromine (neutral and protonated form), the HOMO and LUMO orbitals are  $\pi$ -type orbitals and the electron densities are essentially delocalized over the Theobromine ring.

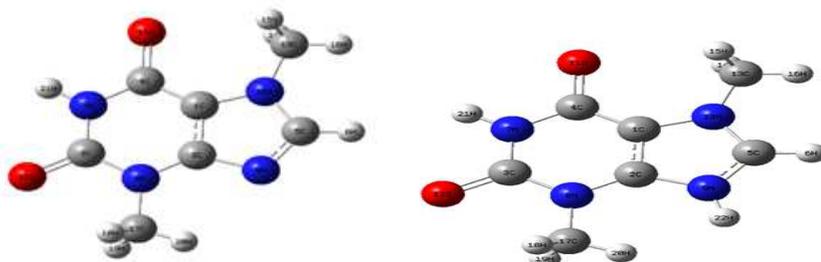


Figure 5. Optimized structures of Theobromine neutral and protonated

	HOMO	LUMO
Theobromine neutral		

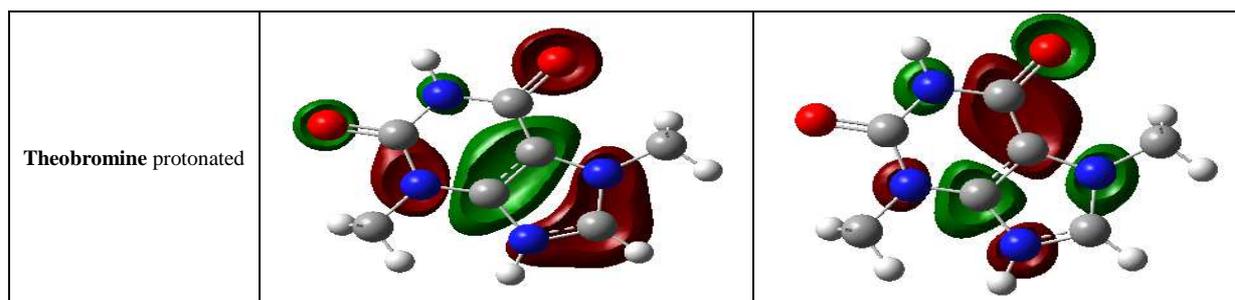
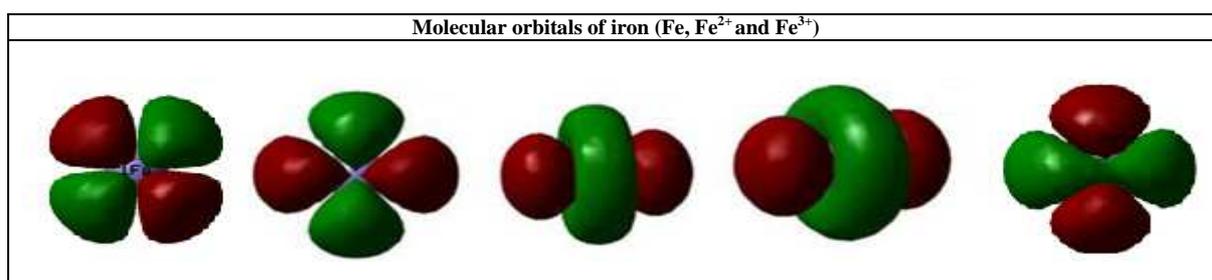


Figure 6. Electron density distribution on Theobromine neutral and protonated molecule HOMO and LUMO

Figure 7. Electron density distribution on Iron: Fe (HOMO and LUMO together), Fe<sup>2+</sup>(HOMO), Fe<sup>2+</sup>(LUMO), Fe<sup>3+</sup>(HOMO) and Fe<sup>3+</sup>(LUMO)



From Table 5., it is clear that the energy gap values follow the order, Theobromine protonated < Fe<sup>2+</sup> < Fe<sup>3+</sup> < Theobromine neutral; which suggested that Theobromine protonated has an ability to donate electrons preferably to Fe<sup>3+</sup> and Fe<sup>2+</sup>. Thus, molecular modelling studies supported well the corrosion inhibition potential of Theobromine protonated while its possible mode of interaction with metal surface.

Table 5. Calculated quantum chemical parameters of the studied compounds

Quantum parameters	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Theobromine neutral	Theobromine protonated
E <sub>HOMO</sub> (eV)	-1.001	-1.765	-0.342	-0.319
E <sub>LUMO</sub> (eV)	-0.705	-1.124	-0.038	-0.027
ΔE <sub>gap</sub> (eV)	0.296	0.641	0.304	0.292

### 3.5. Mechanism of inhibition

The inhibition of mild steel corrosion in 1M HCl solution by the studied inhibitor Theobromine can be explained on the basis of molecular adsorption. This compound inhibits corrosion by controlling both anodic as well as cathodic reactions. It has been reported in literature that inhibitors with donor atoms and highly basic sites can be protonated in acidic solutions [30]. The nitrogen atoms present in the studied inhibitor can readily be protonated in acidic solution. This protonated specie adsorbed can adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic site may occur through  $\pi$ -electrons of aromatic rings and lone pair of electrons of nitrogen and oxygen atoms leading to the decrease in anodic dissolution of mild steel. The inhibitor Theobromine is expected to get adsorbed through the lone pairs of electrons on N atoms, oxygen atoms and delocalized  $\pi$ -electron density on Theobromine rings by their coordination with mild steel surface.

## CONCLUSION

The results obtained lead to the following conclusions:

- (1) Corrosion inhibition was achieved using Theobromine as corrosion inhibitors for mild steel in 1 M HCl at 308K. The highest inhibition efficiency was exhibited by Theobromine, with a value of 90%.
- (2) EIS measurements revealed that the corrosion of mild steel in the absence and presence of the investigated inhibitor was mainly controlled by a charge transfer process.
- (3) Potentiodynamic polarization measurements showed that the Theobromine act as mixed inhibitor types but that they are more pronounced on the cathodic component.
- (4) The adsorptions of Theobromine followed the Langmuir adsorption isotherm, and the adsorption mechanisms of inhibitors on mild steel surface from 1 M HCl occurred chemically and physical adsorptions
- (5) Quantum chemical calculations show that there is a correlation between inhibitive property and molecular parameters.

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