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Cetirizine: A New and Effective Corrosion Inhibitor for Mild Steel in 1 M HCl solution

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Cetirizine was investigated as corrosion inhibitor for mild steel (MS) in 1 M HCl solution by weight loss, electrochemical measurements and quantum chemical calculations. Cetirizine showed 95% inhibition efficiency even at very low concentration of 100 ppm. Polarization study indicates that Cetirizine behaves like a mixed type inhibitor. The adsorption of the inhibitor follows Langmuir adsorption isotherm. The quantum chemical calculations were applied to elucidate adsorption pattern of inhibitor molecules on steel surface.

Keywords: Cetirizine, Mild steel, Weight loss, Electrochemical measurements, Adsorption, Quantum chemical measurements.

1. INTRODUCTION

The corrosion for metals and alloys is a problem of serious concern which considerably affects both economy and safety. Steel is widely used in industries and machinery and many other fields. Acids are used in industries during pickling, cleaning, descaling, etc. [1].Inhibitors are used in acid solution to prevent metal dissolution. The use of organic inhibitors is most effective and most economic method for protection of metallic corrosion. The efficiency of an organic compound as an inhibitor depends on its ability to get adsorbed on the metal surface by replacing water molecule from metal surface [2].

The adsorption of an inhibitor is influenced by the electronic structure of inhibiting molecules, steric factor, aromaticity, electron density at donor site, presence of functional groups, molecular area and molecular weight of the inhibitor molecule [3-4].The adsorption requires the existence of attractive

forces between the adsorbate and the metal [5].Adsorption can be physisorption, chemisorption or a combination of both. [6].Most of the commercially available inhibitors are toxic in nature Thus, the development of non-toxic corrosion inhibitors of natural source and non-toxic type, has been considered to be more important and desirable [7].In recent years researchers have paid attention on the use of drugs as inhibitors for metallic corrosion due to their non-toxic nature, namely Cefatrexyl, Ciprofloxacin, Norfloxacin, Ofloxacin drugs, Tacrine [8-10].Recently, we have studied the inhibiting action of drugs such as Cefotaxime sodium, Cefazolin, Doxycycline, Pheniramine, Streptomycin, Cefalexin, Fexofenadine, Mebendazole, Dapsone, on corrosion of metals in acid media[11-19].We observed that the drugs act as efficient corrosion inhibitors due to the presence of π electrons, hetero atoms in their molecules through which they are either adsorbed or form insoluble metal complex at the metal surface and inhibit metal corrosion[20].Cetirizine drugs are second- generation, non-sedating and long-lasting antihistamines that are now frequently used for the allergic disorders [21].In present work we have investigated the inhibition action of Cetirizine drug as corrosion inhibitor of MS in 1 M HCl using weight loss, electrochemical techniques and quantum chemical calculations.

2. EXPERIMENTAL

2.1. Materials

All the tests were performed on mild steel of following composition (wt. %): 0 .076% C, 0.192% Mn, 0.012% P, 0.026% Si, 0.050% Cr, 0.023% Al, 0.123% Cu and bal. Fe. Specimens with dimensions of 2.5 cm × 2 cm × 0.025 cm were used for weight loss studies. The MS electrode of 8 cm × 1 cm × 0.025 cm sizes with an exposed area of 1 cm^2 and rest being covered by epoxy resin was used as working electrode for electrochemical study.

2.2. Inhibitor

Cetirizine tablets are commercially obtained as a trade name Zyrtec manufactured by the Jordanian Pharmaceutical Manufacturing Company (JPM). The compound is in its purest state, having molecular formula ($C_{21}H_{25}ClN_2O_3$) and melting point (215-220 $^{\circ}C$). Its chemical structure is shown in Fig. 1. All the concentrations of the inhibitor in acid solution, were taken in ppm (parts per million).

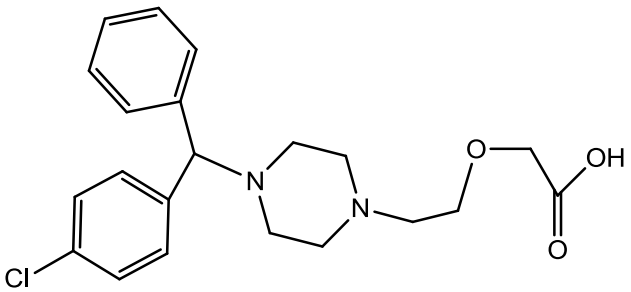

Figure 1. Molecular structure of Cetirizine [2-(2-{4-[(4-chlorophenyl)(phenyl)methyl]piperazin-1-yl}ethoxy)acetic acid] .

2.3. Weight loss measurements

The MS specimens used had a rectangular shape of (2.5 cm ×2.0 cm ×0.025 cm) were abraded with series of emery paper (600-1200 grades) and then washed with distilled water and finally with acetone. After weighing accurately, the specimens were immersed in conical flask which contained 100 ml of 1 M HCl in the absence and presence of different concentration of inhibitor. All the test solutions were kept in a thermostated water bath. After 3 h, the specimens were taken out, washed, dried and weighed accurately. The mean corrosion rate (expressed in mg cm^{-2}) with respect to acid and inhibitor was calculated. All the tests were repeated at different temperatures. The corrosion rate (C_R) was calculated from the following equation,

$$C_R\,(\mathrm{mm/y}) = \frac{87.6W}{atD} \quad (1)$$

where W is the average weight loss of mild steel specimens, a total area of one MS specimen, t is the immersion time (3 h) and D is density of mild steel in (gcm^{-3}). The inhibition efficiency (η%) of inhibitor on the corrosion of MS was calculated as follows,

$$\eta\% = \frac{C_R - {}^{inh}C_R}{C_R}\ \mathrm{X}\ 100 \quad (2)$$

where C_R and ${}^{inh}C_R$ are the corrosion rates of mild steel in the absence and presence of the inhibitors, respectively.

2.4. Electrochemical measurements

Three electrochemical techniques, namely DC-Tafel slope, linear polarization resistance (LPR), and AC-electrochemical impedance spectroscopy (EIS), were used to study the corrosion behavior. All experiments were performed in conventional three electrode cell. Three electrodes connected to Potentiostat/Galvanostat G300-45050 (Gamry Instruments Inc., USA). Echem Analyst 5.0 software package was used for data fitting. The MS was the working electrode, and platinum electrode was used as an auxiliary electrode. All potentials were measured versus a Standard Calomel Electrode (SCE) i.e. reference electrode. Tafel curves were obtained by changing the electrode potential automatically from −0.25 V to +0.25 V versus open corrosion potential at a scan rate of 1.0 mVs^{-1} to study the effect of inhibitor on MS. Linear Polarization Resistance (LPR) experiments were done from −0.02 V to +0.02 V versus corrosion potential at the scan rate of 0.125mVs^{-1}. EIS measurements were performed under potentiostatic conditions in a frequency range from 100 kHz to 0.01 Hz, with amplitude of 10mV AC signal. All experiments were measured after immersion period for 30 min of MS in 1 M HCl in the absence and presence of different concentration of inhibitor.

2.5. Quantum chemical calculations

Quantum chemical calculations were performed using density function theory (DFT) method, B3LYP with electron basis set 6-31G* (d, p) for all atoms. All the calculations were executed with Gaussian 03, E .01.The following quantum chemical indices namely energy of HOMO, LUMO, energy gap, total energy, and dipole moment (μ) was determined [22].

3. RESULTS AND DISCUSSION

3.1. Electrochemical measurements

3.1.1. Potentiodynamic polarization measurements

The data obtained for polarization parameters helps to understand the kinetics of anodic and cathodic reactions for mild steel in 1 M HCl in the absence and presence of different concentration of inhibitor are depicted in Fig. 2. Open corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic slopes (βa and βc) obtained from the Tafel plots are given in Table. 1. The inhibition efficiencies were calculated from I_{corr} values obtained by following equation [23],

$$E\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \quad (3)$$

where I_{corr} and $I_{corr(inh)}$ are the corrosion current density of MS in 1 M HCl in absence and presence of inhibitor.

Table 1. Polarization data for mild steel in 1 M HCl in the absence and presence of different concentration of Cetirizine.

Inhibitor Concentration (ppm)	Tafel Polarization					Linear Polarization	
	E_{corr} (mV vs SCE)	β_a (mV/dec)	β_c (mV/dec)	I_{corr} (μA cm^2)	E%	R_p (Ω cm^2)	E^{R_P} %
Blank	-448	46	96	1070	-	14.0	-
25	-469	90	161	135	87.7	103.1	86.4
50	-470	88	138	120	89.0	155.5	90.9
75	-479	75	130	95	91.3	238.3	94.1
100	-483	49	64	50	95.4	294.5	95.2

If the displacement in corrosion potential values is 85 mV in inhibited solution with respect to uninhibited solution, then the inhibitor can be said to be cathodic or anodic[24]. For Cetirizine, no definite trend was observed in the shift of values (barely 21-35 mV) of open corrosion potential (E_{corr}), which suggested that it is a mixed type inhibitor [25]. The values of corrosion current densities (I_{corr}) and polarization resistance (R_p) are given in Table 1. The values of I_{corr} decreases and R_p values increase as the concentration of inhibitor increases suggesting the retardation of steel corrosion in the presence of inhibitor in 1 M HCl solution.

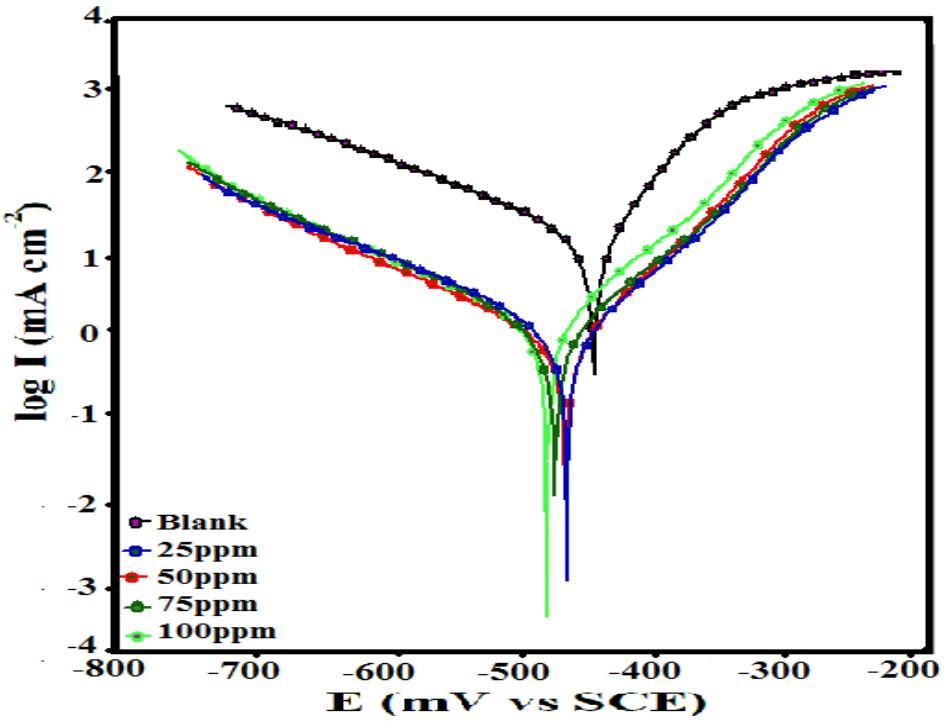

Figure 2. Polarization curves for mild steel in 1 M HCl in absence and presence of different concentration of Cetirizine.

3.1.2. Electrochemical impedance spectroscopy (EIS)

The role of Cetirizine on impedance Bode plot, phase angle plot and equivalent circuit for mild steel in 1 M HCl is shown in Fig. 3-4.The typical Nyquist plot of the mild steel in 1 M HCl solution gives a semi-circle loop. The diameter of the semicircles increases with increasing concentration of inhibitor. The values of double layer capacitance, C_{dl} was calculated from equation [26],

$$C_{dl} = Y_0(\omega_{max})^{n-1} \quad (4)$$

where Y_0 is CPE coefficient, n is CPE exponent (phase shift), ω is the angular frequency. All the data obtained are listed in Table 2.

Table 2. Electrochemical impedance parameters and corresponding efficiencies of MS in 1 M HCl at different concentration of Cetirizine.

Inhibitor Concentration(ppm)	R_{ct} (Ω cm^2)	n	Y_o ($10^{-6}\Omega^{-1}$ cm^{-2})	Cdl (μF cm^{-2})	E%
Blank	12.1	0.868	242.6	100.6	-
25	109.2	0.847	102.4	43.9	88.7
50	129.2	0.863	79.4	39.7	90.5
75	194.1	0.865	78.9	38.9	93.6
100	219.2	0.853	77.6	38.7	95.0

In case of electrochemical impedance spectroscopy, the inhibition efficiency was calculated using charge transfer resistance (R_{ct}) as follow,

$$E\% = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (5)$$

where $R_{ct(inh)}$ and R_{ct} are the values of charge transfer resistance in presence and absence of inhibitor in 1 M HCl respectively. The data in Table 2 shows that by increasing the concentration of inhibitor, the R_{ct} values increases, while the C_{dl} values decreases. The higher values of R_{ct} are generally attributed to slower rate of corrosion of mild steel. The decrease in the values of C_{dl} might result from the lowering of general dielectric constant or from the increase in thickness of the electrical double layer, which suggests the adsorption of inhibitor molecules on mild steel surface [27].

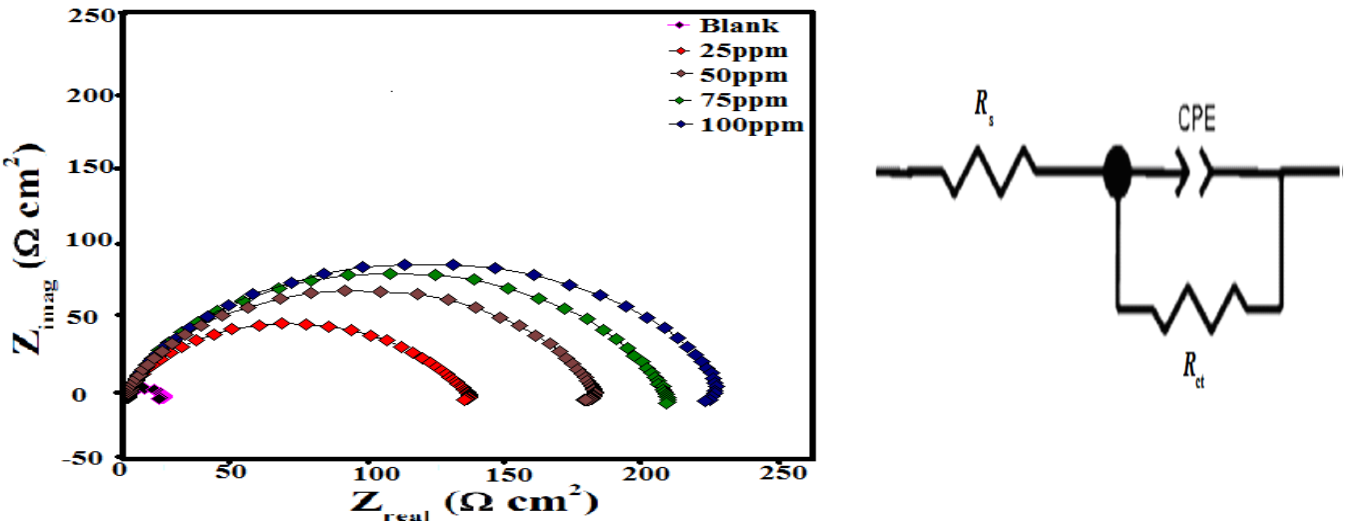

Figure 3: The **(a)** Nyquist plot for mild steel in 1M HCl and different concentrations of Cetirizine and **(b)** Equivalent circuit used for simulation of data.

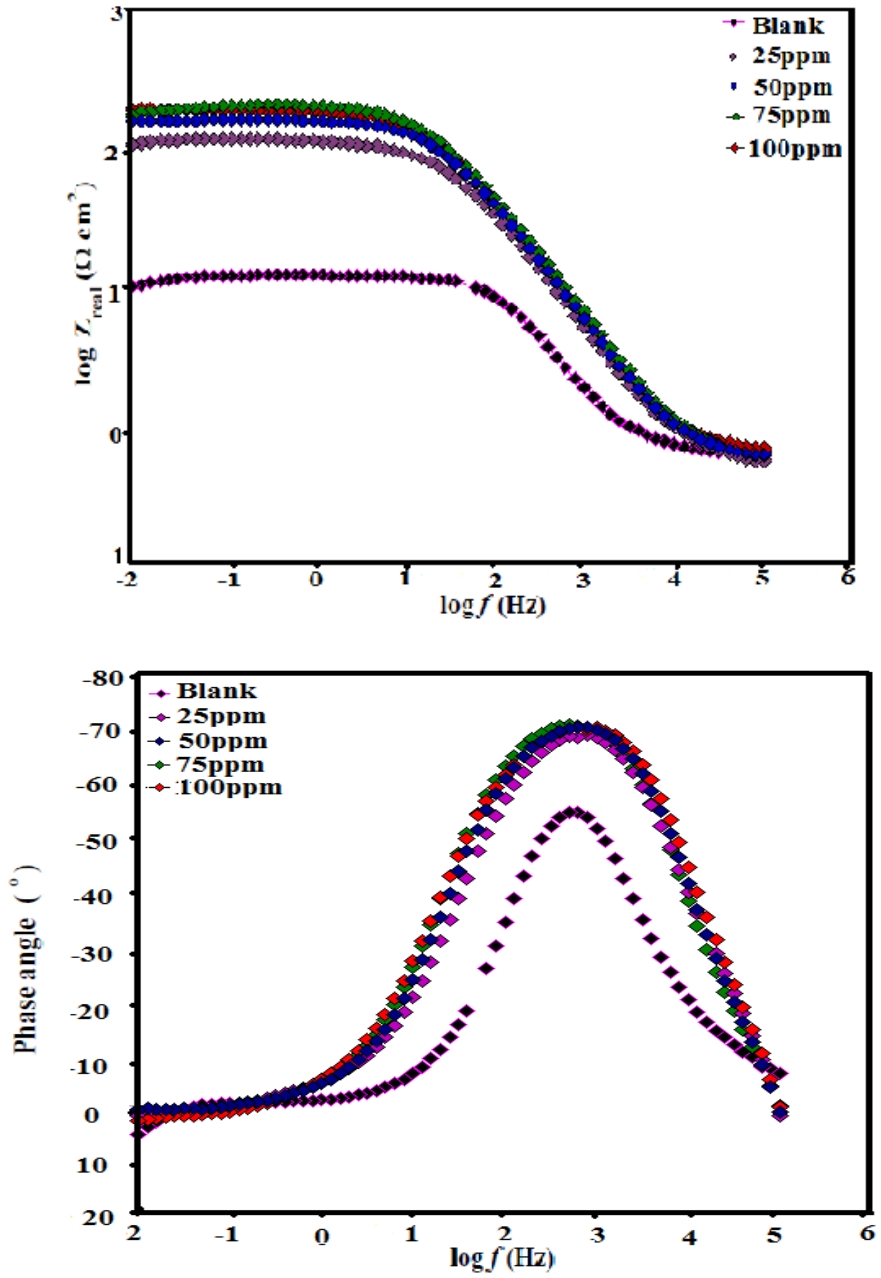

Figure 4. (a) Bode-impedance and **(b)** Phase angle plots for mild steel in 1 M HCL and different concentration of Cetirizine.

3.2. Weight loss measurements

The weight loss results obtained for mild steel in 1 M HCl in the presence and absence of different concentration of Cetirizine are summarized in Table 3. The corrosion rate (mg cm^{-2}) values of mild steel in 1 M HCl decreases as the concentration of inhibitor increases i.e. the inhibition efficiency increases as the concentration of inhibitor is raised.

Table 3. Weight loss measurements for MS in 1 M HCl at different concentrations of Cetirizine

Inhibitor concentration (ppm)	Weight loss ($mgcm^{-2}$)	η%	CR (mm/y)	θ
Blank	20.00	-	74.20	-
25	3.00	85.71	11.13	0.85
50	2.10	90.00	7.79	0.90
75	1.50	92.82	5.56	0.92
100	0.90	95.71	3.33	0.95

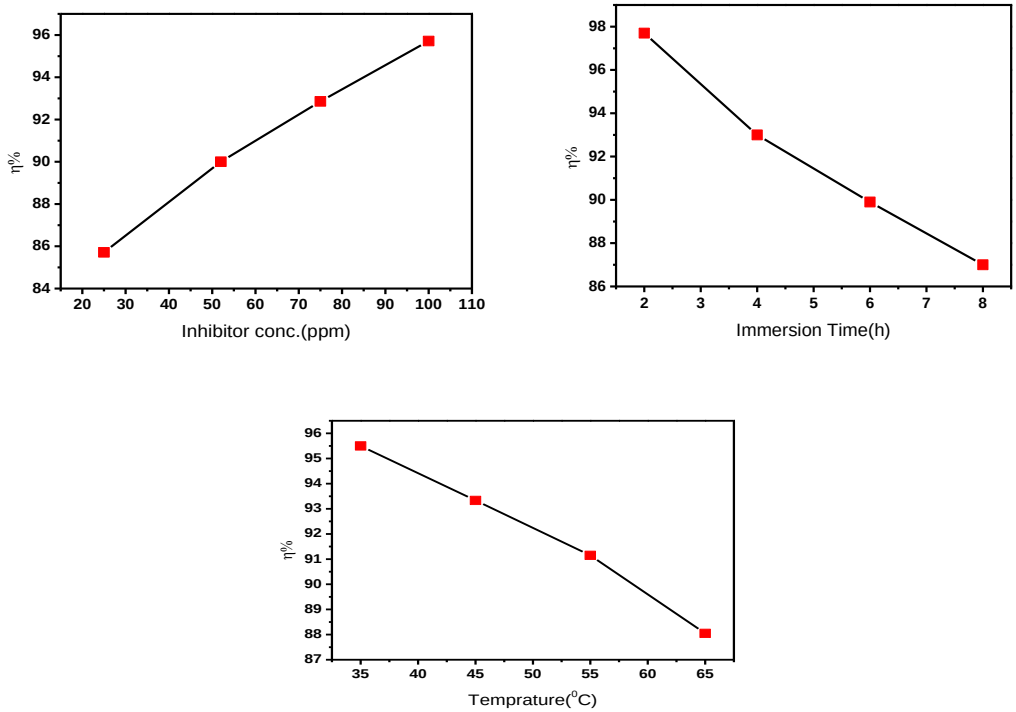

Figure 5. Variation of inhibition efficiency in 1M HCl on mild steel with (A) different concentrations of Cetirizine; (B) different immersion time; (C) different temperatures from the weight loss data.

3.2.1. Adsorption isotherm

The adsorption isotherms provide useful information for the mechanism of corrosion inhibition. The surface coverage, θ, was calculated from the equation,

$$\theta = \frac{C_R - {}^{inh}C_R}{C_R} \qquad (6)$$

where, C_R and ${}^{inh}C_R$ are the corrosion rates of mild steel in the absence and presence of Cetirizine respectively. By fitting the θ values obtained from weight loss data to various isotherms namely Langmuir, Temkin, and Frumkin, the best fit was obtained with the Langmuir isotherm [28]. A straight line was obtained on plotting (C/θ) vs θ for Langmuir isotherm with regression coefficient (R^2= 0.99974) confirm this approach as shown in Fig.6 for all the techniques used.

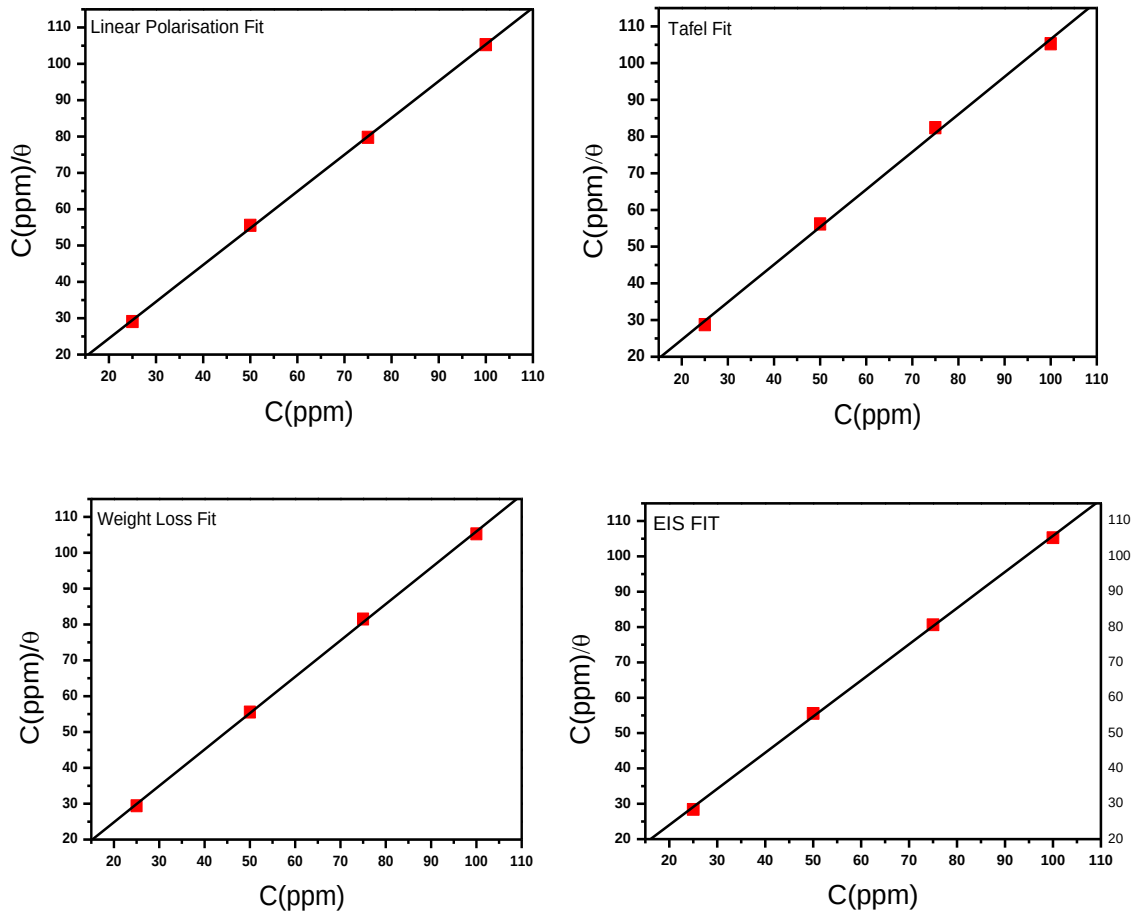

Figure 6. The Langmuir adsorption isotherm plots for mild steel at different concentrations of Cetirizine by different methods.

3.2.2. Thermodynamic activation parameters

A plot of the logarithm of corrosion rate vs 1000/T gives a straight line as shown in Fig. 7(a). The apparent activation energy (E_a) was calculated by using following equation [29]:

$$\ln(C_R) = \frac{-E_a}{RT} + A \qquad (7)$$

where E_a is activation energy for the corrosion of mild steel in 1 M HCl, R is the molar gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. The Values of E_a in

1 M HCl in absence and presence of Cetirizine were determined from the slope by plotting the values obtained and are presented in Table 4.

Table 4. Thermodynamic parameters for mild steel in 1 M HCl in absence and presence of Cetirizine

Inhibitor conc. (ppm)	E_a ($kJmol^{-1}$)	ΔH^* ($kJmol^{-1}$)	ΔS^* ($Jmol^{-1}\ K^{-1}$)	ΔQ_{ads} ($kJmol^{-1}$)
Blank	38.15	35.47	-93.62	-
100	66.02	63.34	-28.77	-27.10

The addition of Cetirizine changed the values of E_a, and may be attributed to the adsorption of inhibitor on mild steel surface causing an energy barrier.

The enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) were calculated from the equation;

$$C_R = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \quad (8)$$

Where h is Planck constant, N is Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. Fig. 7(b) shows a plot of log (C_R /T) against 1000/T which gave straight lines with slope of (-ΔH^*/R) and intercept of [(ln(R/Nh)) + (ΔS^*/R)] from which the values of ΔH^* and ΔS^* were calculated and are given in Table 4. Positive sign of ΔH^* reflects the endothermic nature of dissolution of steel. The values of ΔS^* were higher in presence of inhibitors than in its absence suggesting that the randomness increases on going from reactants to activated complex [30].

The heat of adsorption (ΔQads) was obtained from the surface coverage and temperature by using following equation,

$$Log\left(\frac{\theta}{1-\theta}\right) = LogA + LogC_{inh} - \left(\frac{\Delta Q_{ads}}{2.303RT}\right) \quad (9)$$

A plot of $Log\left(\frac{\theta}{1-\theta}\right)$ vs $1/T$ is given in Figure 7c. The value of heat of adsorption was determined from the slope $\left(\frac{-\Delta Q_{ads}}{2.303RT}\right)$ of the graph. The value of heat of adsorption is given in Table 4. It is evident from the Table 4 that (ΔQ_{ads}) has negative value which indicates that inhibitor adsorption decreases with increase in the temperature hence decrease in inhibitor efficiency. The negative value of (ΔQ_{ads}) also suggested that the adsorption of inhibitor is an exothermic process [31].

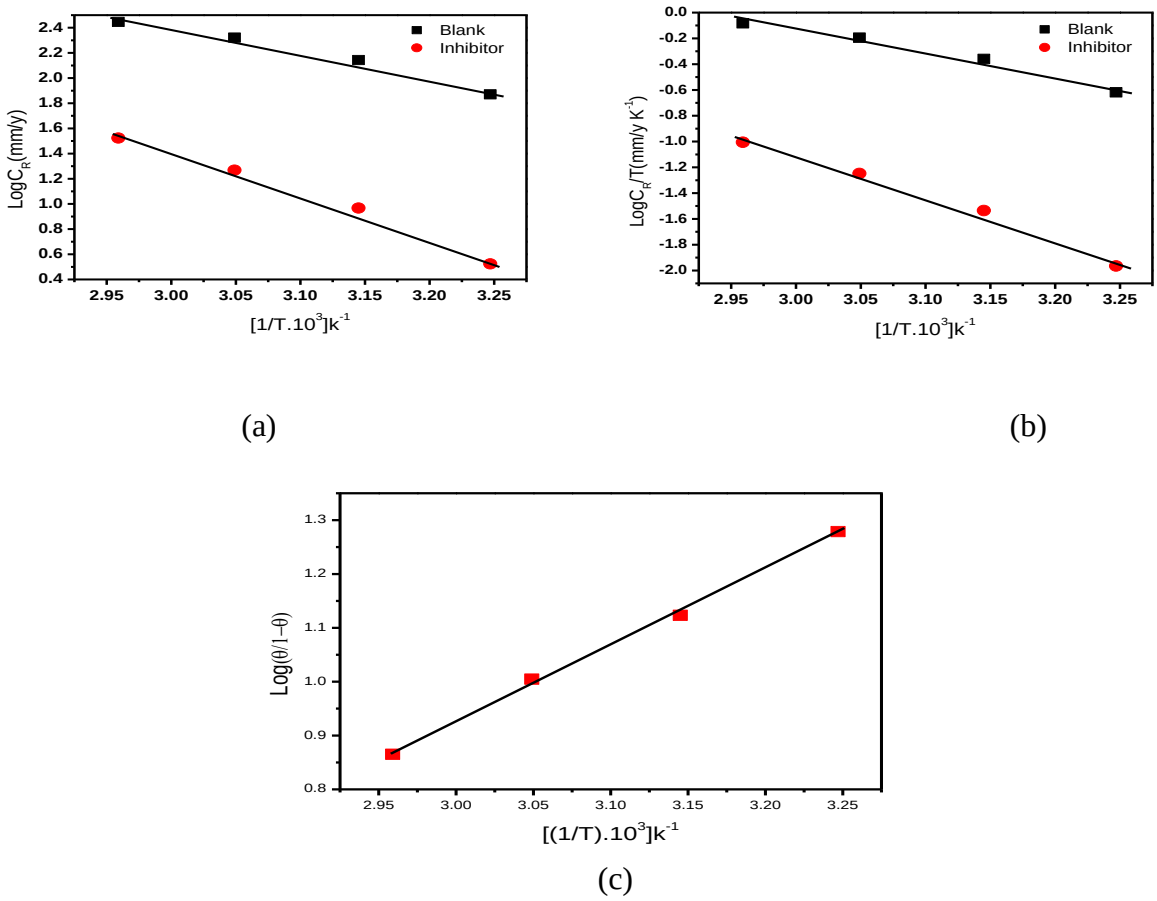

Figure 7. (a) Arrhenius plot of log CR vs. 1000/T (b) Transition state plot of log CR/T vs. 1000/T (c) $Log\left(\frac{\theta}{1-\theta}\right)$ versus 1/T for MS in 1M HCl in the absence and the presence Cetirizine.

The standard free energy of adsorption, $\Delta G°_{ads}$ and the values of equilibrium constant, K_{ads} at different temperatures were calculated from the equation;

$$K = \frac{\theta}{C(1-\theta)} \tag{10}$$

$$\Delta G^{\circ}_{ads} = -RT\ln(55.5K_{ads}) \tag{11}$$

The value 55.5 in the above equation is the concentration of water in solution in mol/lit. The values of ΔG_{ads} are given in Table 5.

The negative values of ΔG_{ads} indicate the spontaneity of the adsorption of inhibitor molecules on the metal surface. Generally, the values of ΔG_{ads} up to -20 KJ mol^{-1} are consistent with the electrostatic interaction (physisorption) of charged molecules and the charged metal, while those around -40 KJ mol^{-1} or more negative are associated with sharing or transfer of electrons from inhibitor molecules to the metal surface forming coordinate type bond (chemisorption)[32]. The

calculated values of ΔG_{ads} obtained range from -39.06 to -40.12 KJ mol^{-1}, indicating that the adsorption of the inhibitor on mild steel surface is by chemical adsorption [33].

Table 5. Standard free energy of adsorption of mild steel in 1M HCl in absence and presence of Cetirizine at different temperatures

Temperature(ºC)	$-\Delta G_{ads}$ (kJ mol^{-1})
35	39.00
45	39.32
55	39.81
65	40.12

3.3. Quantum Chemical Calculations

The structure and electronic parameters were obtained by means of theoretical calculations using the computational methodologies of quantum chemistry. The optimized molecular structures and frontier molecular orbital density distribution of the studied molecule and shown in Fig.8. The calculated quantum chemical parameters such as E_{HOMO}, E_{LUMO}, $\Delta E_{LUMO-HOMO}$, dipole moments (μ) are listed in Table 6. The molecular structure of Cetirizine shows that the molecules seems to adsorb on mild steel surface by sharing of electrons of the nitrogen atoms with iron to form coordinated bonds and π-electron interactions of the aromatic rings.

Table 6. Calculated quantum chemical parameters of Cetirizine.

Quantum Parameters	Cetirizine
HOMO (hartree)	-0.1637
LUMO (hartree)	0.0139
ΔELUMO-HOMO (hartree)	0.1777
Dipole Moment (μ)	4.2286

The high value of highest occupied molecular orbital, E_{HOMO} indicates the tendency of the molecule to donate electrons to acceptor molecule with empty and low energy orbital. Therefore, the energy of the lowest unoccupied molecular orbital, E_{LUMO} indicates the tendency of the molecule to accept electrons.

The lower the value of E_{LUMO}, the more probably the molecule would accept electrons [34]. The energy gap ΔE is an important parameter which is related to reactivity of the inhibitor molecule towards the metal surface.

The interaction of inhibitor molecule to the metal surface is related to transfer of electrons from inhibitor to metal surface [35].

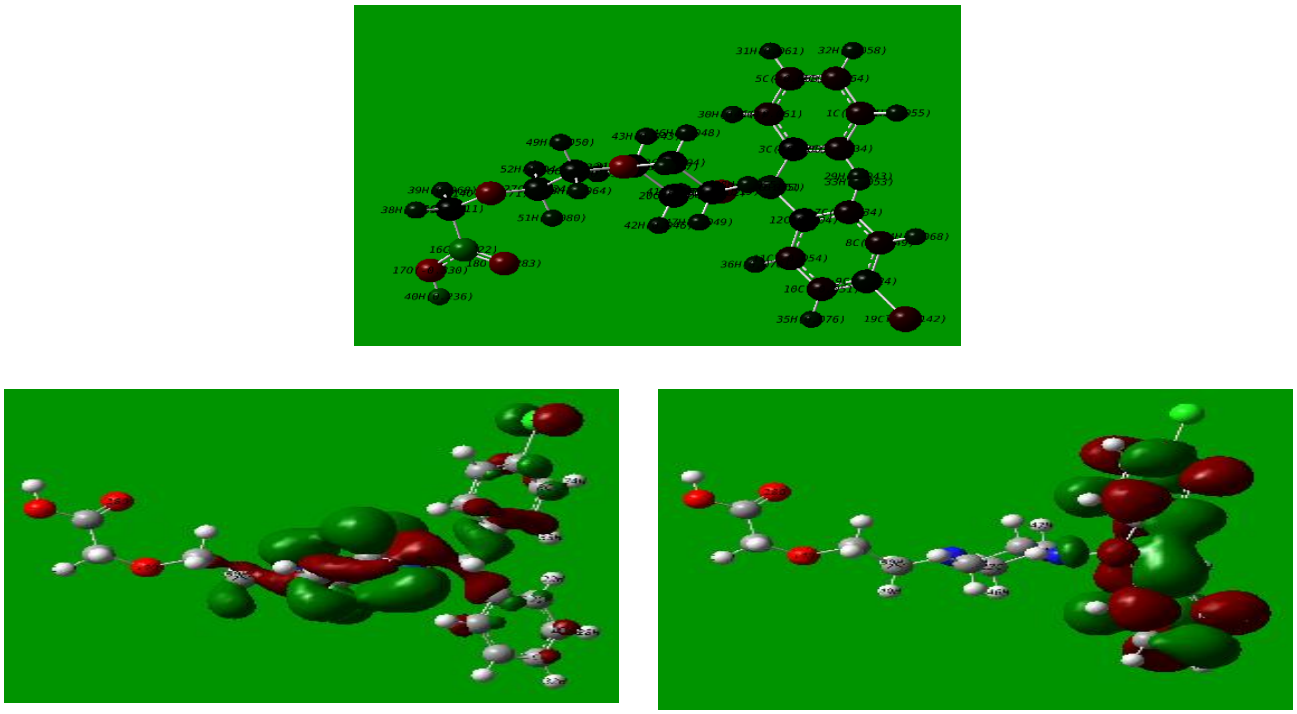

Figure 8. Optimized molecular structure and frontier molecular orbital density distribution of Cetirizine.

3.4. Mechanism of adsorption and inhibition

The data obtained from the different methods conclude that the inhibition by Cetirizine might due to adsorption at the metal/solution interface. The essential effect of Cetirizine

Used as corrosion inhibitor is due to the presence of free electron pairs in the oxygen and the nitrogen atoms, π-electrons on the aromatic rings, molecular size, and mode of interaction with the metal surface and the formation of metallic complexes. The unshared and π-electrons interact with d-orbital of Fe to provide a protective film. The inhibitive properties of such compounds depend on the electron densities around the active centre; the inhibition mechanism of the inhibitor is a combination of surface blockage and electrostatic repulsion between adsorbed surfactant layer and chloride ions [36]. The adsorption density of inhibitor depends on the inhibitor concentration. The inhibition of these reactions would obviously depend on the degree of the surface coverage of the metal with the adsorbate. Adsorption is assumed to occur on the surface of the metal between the aggressive Cl^- and the inhibitor molecules, on the other. The order of the increasing inhibition, the molecular size of the inhibitor and consequently the number of adsorption centres plays an important role in the enhancement of the protection of carbon steel against corrosion [37].

4. CONCLUSIONS

1**.** Cetirizine is good inhibitor for mild steel in 1M HCl. The inhibition efficiency increased with increasing the concentration of the inhibitor up to a maximum of 95% at 100ppm.

2. Polarization curves indicated that Cetirizine is a mixed- type inhibitor. The inhibition efficiencies obtained from polarization and EIS were in good agreement.

3. The adsorption of inhibitor molecules on the mild steel surface in 1M HCl solution follow Langmuir adsorption isotherm.

4. The negative values of ΔG_{ads} show the spontaneity of the adsorption.

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