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Cimetidine as an Effective Corrosion Inhibitor for Mild Steel in Hydrochloric Acid

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The performance of Cimetidine (2-cyano- 1-methyl- 3-(2-[(5-methyl- 1*H*-imidazol- 4-yl)methylthio]ethyl)guanidine) as corrosion inhibitor for mild steel in 1 M HCl was thoroughly investigated by weight loss and electrochemical methods. The inhibition efficiency of cimetidine obtained by all methods was in good agreement with each other. Polarization studies revealed that the inhibiting action of the cimetidine is under mixed control. The free energy of adsorption and the influence of temperature on the adsorption of inhibitor onto mild steel surface have been reported. The quantum chemical calculations were applied to elucidate adsorption pattern of inhibitor molecules on the steel surface.

Keywords: Cimetidine, Corrosion Inhibitor, Mild Steel, Hydrochloric acid

1. INTRODUCTION

Despite the wide range of available organic compounds, the final choice of the inhibitor for a particular application is restricted by several factors, including increased environmental awareness and the need to promote environmentally friendly processes, coupled with the specificity of action of most acid inhibitors, which often necessitates the combined action of compounds to achieve effective corrosion inhibition. Consequently, there exists a need to develop inexpensive and environmental friendly inhibitors. In recent years researchers have paid attention to the development of drugs as inhibitors for the corrosion of metals in acid media [1-13].

The aim of the present work is to study the cimetidine (2-cyano- 1-methyl- 3-(2-[(5-methyl- 1*H*-imidazol- 4-yl)methylthio]ethyl)guanidine) as corrosion inhibitor for mild steel in 1 M HCl solution using weight loss and electrochemical techniques. Cimetidine is a histamine H_2-receptor antagonist that inhibits stomach acid production. It is largely used in the treatment of heartburn and peptic ulcers. It reduces the amount of acid production in the stomach. There is no report on use of Cimetidine as a corrosion inhibitor in hydrochloric acid. No concrete report is seen for the employment of this compound as corrosion inhibitor in 1 M HCl medium. The effect of temperature on different concentrations of inhibitor has been analyzed. Thermodynamic parameters of the corrosion reaction have been obtained for the above studies.

2. EXPERIMENTAL

2.1 Materials

The mild steel coupons of rectangular size (2.5 × 2.0 × 0.025) cm having the composition ; (wt %): C 0.17%; Mn 0.46%; Si 0.026%; Cr 0.050%; P 0.012%; Cu 0.135%; Al 0.023%; Ni 0.05%; and balance Fe were used for weight loss studies. Pretreatment of mild steel coupons included abrasion with emery paper from 600 to 1200 grade. The specimens were washed thoroughly with double distilled water and finally degreased with acetone and dried at room temperature. The aggressive solution 1 M HCl was prepared by dilution of analytical grade HCl (37%) with double distilled water and all experiments were carried out in unstirred solutions. Cimetidine was procured from Zydus Cadilla Pharmaceuticals Limited. IUPAC name of cimetidine is 2-cyano- 1-methyl- 3-(2-[(5-methyl- 1*H*-imidazol- 4-yl)methylthio]ethyl)guanidine and its molar mass is 252.34 g/mol.

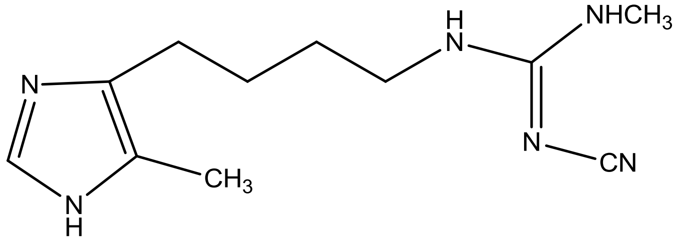

Figure 1. Molecular structure of Cimetidine (2-cyano- 1-methyl- 3-(2-[(5-methyl- 1*H*-imidazol- 4-yl)methylthio]ethyl)guanidine)

2.2 Procedures

2.2.1 Weight loss measurements

For weight loss experiments, clean weighed metal rectangular coupons were immersed in 100 ml of 1 M HCl solution in conical flasks for 3 hours at 308 K temperature. Every sample was weighed by an electronic balance, and then placed in the acid solution (100 mL). The duration of the immersion was 3 hours at the temperature range from 308 to 338 K. After immersion, the surface of the specimen was cleaned by double distilled water followed rinsing with acetone and the sample was weighed again in order to calculate inhibition efficiency (η%) the corrosion rate (C_R). The inhibition efficiency and surface coverage (θ) was determined by using following equation:

$$\theta = \frac{w_0 - w_i}{w_0} \quad (1)$$

$$\eta\% = \frac{w_0 - w_i}{w_0} \times 100 \quad (2)$$

where, w_i and w_0 are the weight loss values in presence and absence of inhibitor, respectively.

The corrosion rate (C_R) of mild steel was calculated using the relation:

$$C_R\ (mm/y) = \frac{87.6 \times w}{atD} \quad (3)$$

where, w is corrosion weight loss of mild steel (mg), a the area of the coupon (cm^2), t is the exposure time (h) and D the density of mild steel (g cm^{-3}).

2.2.2 Electrochemical measurements

The electrochemical studies were made using a Gamry three electrode cell assembly at room temperature (308 K). The mild steel of 1.0 × 1.0 cm was the working electrode, platinum electrode was used as an auxiliary electrode, and standard calomel electrode (SCE) was used as reference electrode. The working electrode was polished with different grades of emery papers, washed with water and degreased with acetone. All electrochemical measurements were carried out using Gamry Potentiostat/Galvanostat (Model G-300) with EIS software Gamry Instruments Inc., USA. Gamry applications include software DC 105 for corrosion and EIS 300 for EIS measurements and Echem Analyst version 5.50 software packages for data fitting. Prior to the electrochemical measurement, a stabilization period of 30 minute was allowed, which was proved to be sufficient to attain a stable value of $E_{corr.}$

Tafel curves were obtained by changing the electrode potential automatically from −250 to +250 mV versus corrosion potential (E_{corr}) at a sweep rate of 1 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion current densities (I_{corr}).EIS measurements were carried out in a frequency range from 100 kHz to 0.00001 kHz under potentiodynamic conditions, with amplitude of 10 mV peak-to-peak, using AC signal at E_{corr}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$\eta\% = \frac{I^{0}_{\mathrm{corr}} - I^{'}_{\mathrm{corr}}}{I^{0}_{\mathrm{corr}}} \times 100 \qquad (4)$$

where, I^{0}_{corr} and $I^{\mathrm{i}}_{\mathrm{corr}}$ are the corrosion current in absence and in presence of inhibitor, respectively. The charge transfer resistance values were obtained from the diameter of the semi circles of the Nyquist plots. The inhibition efficiency of the inhibitor has been found out from the charge transfer resistance values using the following equation:

$$\eta\% = \frac{R^{'}_{\mathrm{ct}} - R^{0}_{\mathrm{ct}}}{R^{'}_{\mathrm{ct}}} \times 100 \qquad (5)$$

where, R^{0}_{ct} and $R^{'}_{\mathrm{ct}}$ are the charge transfer resistance in absence and in presence of inhibitor, respectively. All electrochemical measurements were done in unstirred and non de-aerated solutions.

2.3. 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, and dipole moment (μ) was determined [14].

3. RESULTS AND DISCUSSIONS

3.1 Weight loss studies

3.1.1 Effect of inhibitor concentration

The cimetidine drug showed maximum inhibition efficiency of 95 % in HCl at an optimum concentration of 500 ppm. Further increase in inhibitor concentration did not cause any significant change in the performance of the inhibitor. The values of percentage inhibition efficiency (η%) and corrosion rate (C_R) obtained from weight loss method at different concentrations of cimetidine at 308 K are summarized in Table 1.

Table 1. Parameters obtained from gravimetric measurements for mild steel in 1 M HCl containing different concentrations of cimetidine at 308 K

Inhibitor	Concentration (ppm)	Corrosion rate (mm y^{-1})	Surface coverage (θ)	η (%)
Blank	0.0	77.9	--	--
Cimetidine	100	19.2	0.753	75.3
	200	9.3	0.880	88.0
	500	3.4	0.956	95.6

From table 1 it is clear that increase of inhibitor concentrations caused a decrease in the weight loss as well as corrosion rate of mild steel.

3.1.2. Effect of temperature

The effect of temperature on the inhibition efficiency of the cimetidine for mild steel in 1 M HCl solution in the absence and presence of optimum concentration (ppm) at temperature ranging from 308 to 338 K was investigated by weight loss measurements. The results obtained are given in Table 2 and plot between different temperatures vs. efficiency is shown in Figure 2

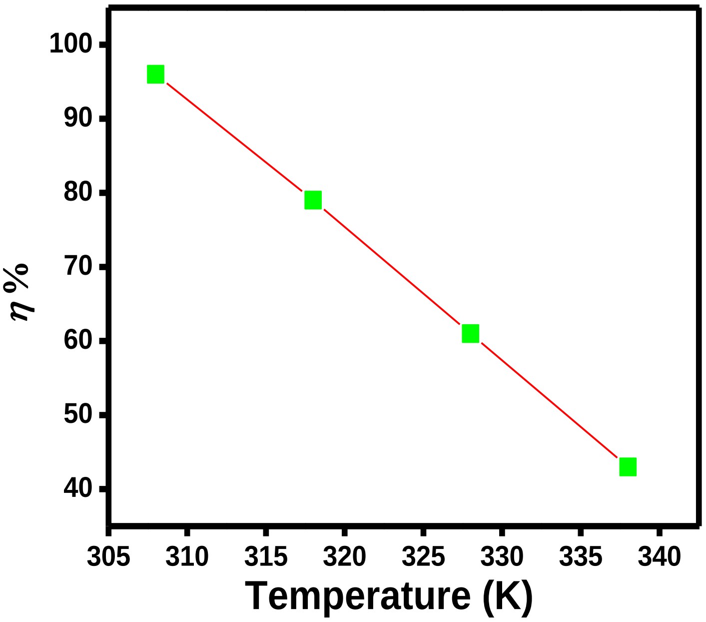

Figure 2. Variation of inhibition efficiency with Temperature

It is observed that as the temperature increases from 308 to 338 K inhibition efficiency decreases while corrosion rate increases. This behavior can be explained on the basis that the increase in temperature causes desorption of the inhibitor molecules from the surface of mild steel.

3.1.3. Thermodynamic activation parameters

In order to find the activation parameters of inhibition process for mild steel in 1 M HCl solution, weight loss measurements were performed at a temperature range 308 K to 338 K in the absence and presence of 500 ppm cimetidine. A plot of the logarithm of the corrosion rate (mmy^{-1}) of mild steel vs. 1000/*T* gave a straight line as shown in Figure 3a.

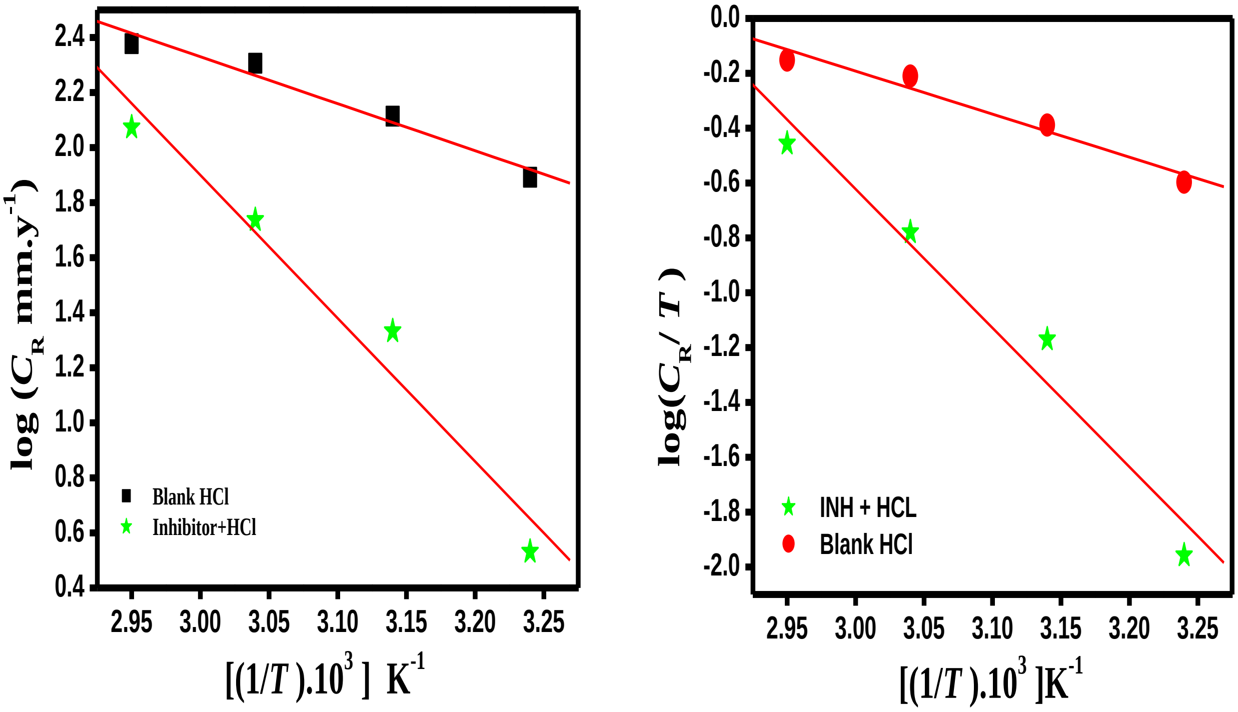

Figure 3. Arrhenius plot of (a) log C_R vs. 1000/T (b) log (C_R/T) versus 1000/T in 1 M HCl in absence and presence of different concentration of cimetidine

According to the Arrhenius equation:

$$C_R = A\exp\left(\frac{-E_a}{RT}\right) \tag{6}$$

where E_a is the apparent activation energy for the corrosion of mild steel in 1 M HCl solution, R gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. The values of E_a obtained from the slope of the line (Figure 3a) are given in Table 2.

The straight lines were obtained according to the transition state equation:

$$C_R = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{H^*}{RT}\right) \tag{7}$$

where N is the Avogadro's number, h the Planck's constant, $\Delta H^*$the enthalpy of activation and $\Delta S^*$the entropy of activation. Figure 3b shows a plot of log (C_R/T) versus 1000/T gives a straight line with a slope of ($-\Delta H^*$/2.303 R) and an intercept of log (R/Nh + ΔS^*/2.303 R) from which the values of $\Delta H^*$and $\Delta S^*$are calculated and are given in Table 2.

Table 2 shows that value of enthalpy of activation is positive and higher in presence of inhibitor. The positive sign of ΔH^*reflects the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow. The entropy of activation $\Delta S^*$is higher (-76.41 JK^{-1}mol^{-1}) in presence of inhibitor than that (-136.4 JK^{-1}mol^{-1}) in the absence of the inhibitor. This is opposite to what would be expected, since adsorption of inhibitor is an exothermic process and is always accompanied by a decrease of entropy.

Table 2. Thermodynamic parameters for mild steel in 1 M HCl in absence and presence of optimum concentration (100 ppm) of investigated cimetidine

Solutions	Temperature	$-\Delta G^{o}_{ads}$	K_{ads}	E_a	ΔH^*	ΔS^*
	(K)	(kJ mol^{-1})	(10^3 M^{-1})	(kJmol^{-1})	(kJmol^{-1})	(J K^{-1}mol^{-1})
Blank		-	-	28.0	22.4	-136.4
Cimetidine				100.5	98.1	-76.41
	308	35.42	182.73			
	318	32.69	42.14			
	328	32.01	22.53			
	338	31.34	12.53			

The reason could be explained as follows: the adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compound in the aqueous phase [$Org_{(sol)}$] and water molecules at the electrode surface [$H_2O_{(ads)}$]. In this situation, the adsorption of organic inhibitor is accompanied by desorption of water molecules from the surface. Thus, while the adsorption process for the inhibitor is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. The thermodynamic values obtained are the algebraic sum of the adsorption of organic molecules and desorption of water molecules. Therefore, the gain in entropy is attributed to the increase in solvent entropy [15]. The positive values of ΔS^*means that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of inhibitor onto the mild steel surface [16].

3.1.4. Adsorption considerations

The standard free energy of adsorption ($\Delta G°_{ads}$) at different temperatures is calculated from the equation:

$$\Delta G^{o}_{ads} = -RT\ln(55.5K_{ads}) \tag{8}$$

where, the value 55.55 is the concentration of water in solution expressed in M [17-18] and K_{ads} is equilibrium adsorption constant and is given by:

$$K_{ads}C = \frac{\theta}{1-\theta} \tag{9}$$

where, θ is degree of surface coverage of the mild steel surface and C the molar concentration of inhibitor. The values of K_{ads} and $\Delta G°_{ads}$ for mild steel in 1 M HCl solution in the presence of 500 ppm cimetidine is given in Table 2.

The negative values of ΔG^{o}_{ads} ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface. Generally, values of ΔG^{o}_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and charge metal, such as physisorption. When it is around -40 kJ mol^{-1}or higher values it involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond that is chemisorption [19-20]. The calculated values range from -31.34 to-35.42 kJmol^{-1} (Table 2). The unshared electron pairs of heteroatom interact with d-orbital of iron atom of steel to provide a protective chemisorbed film [21].

3.2. Electrochemical measurements

3.2.1. AC technique: Electrochemical impedance spectroscopy

AC impedance results of mild steel/hydrochloric acid interface obtained in the absence and in the presence of various concentrations of cimetidine in the form of Nyquist plots are shown in Figure 4.

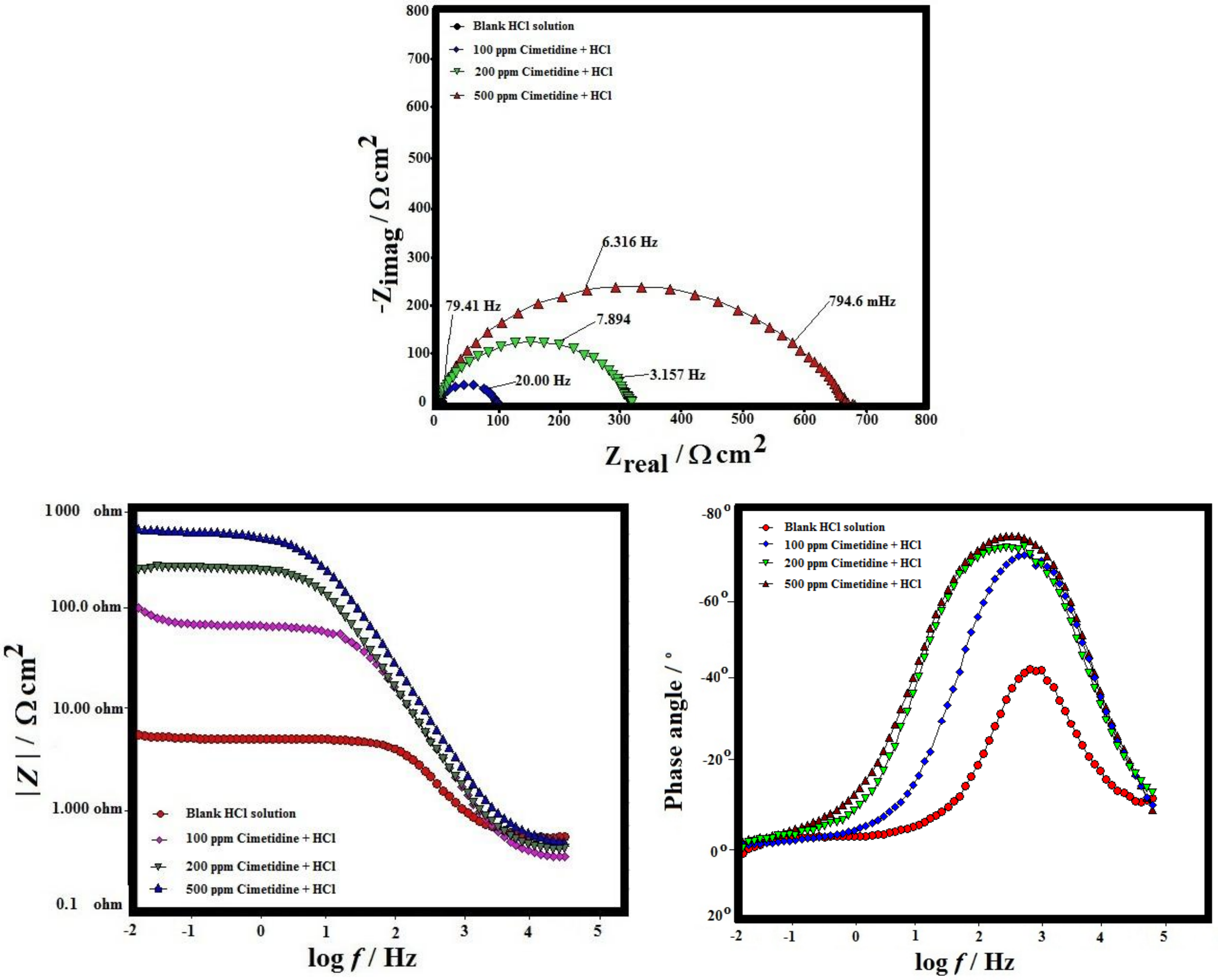

Figure 4. Nyquist plots for mild steel in 1 M HCl in absence and presence of various concentrations of cimetidine at 308 K

The Nyquist plots for cimetidine characterized by one semicircular capacitive loop. The corrosion process is two steps as in any electrochemical process. First, the oxidation of the metal (charge transfer process) and second, the diffusion of the metallic ions from the metal surface to the solution (mass transport process). Inhibitors get adsorbed on the electrode surface and thereby produce a barrier which inhibits corrosion [22].

It must be noted that the capacitive loops are depressed ones with centers under the real axis even though they have a semicircle appearance. This kind of deviations is mostly referred to as frequency dispersion which is attributed to irregularities and heterogeneities of the solid surfaces [23]. In the real corrosion systems, the metal/solution interface double layer does not behave as a real capacitor. The charge distribution is controlled by electron on the metal side of the double layer, whereas it is controlled by ions on the solution side [24] The high frequency (HF) part of the impedance and phase angle reflects the behavior of heterogeneous surface layer, whereas the low frequency (LF) part shows the kinetic response for the charge transfer reaction [25]. The equivalent circuit used is shown in Figure 5.

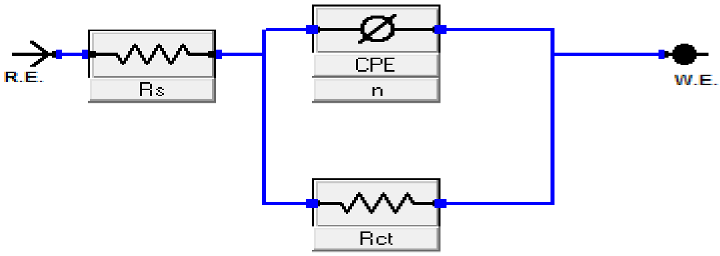

Figure 5. Equivalent circuit used to fit the EIS data

Table 3. Electrochemical Impedance Spectroscopy measurements on mild steel electrode in 1 M HCl in absence and presence of different concentration of cimetidine at 308 K

Inhibitor	R_s (Ω)	R_{ct} (Ω cm^2)	n	Y_0 (μFcm^{-2})	θ	η (%)
Blank	1.20	13.6	0.827	250.1	--	--
100	1.07	109.4	0.838	126.1	0.875	87.5
200	1.30	315.4	0.811	72.5	0.955	95.5
500	1.06	660.1	0.842	74.8	0.979	97.9

This consist of the solution resistance, R_s, in series with the parallel combination of constant phase element (CPE) in place of double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}).

Mathematically, a CPE's impedance is given by

$$Y_{\mathrm{CPE}} = Y_0 (j\omega)^n \tag{10}$$

where Y_0 is the amplitude comparable to a capacitance, j is the imaginary unit, ω is the angular frequency ($\omega = 2\pi f$, the frequency in Hz), and n is the phase shift which gives details about the degree of surface in homogeneity. The CPE can be expressed by the values of n if resistance (n=0, Y_0 = R), capacitance (n=1, Y_0 = C), inductance (n= -1, Y_0 = L) and Warburg impedance (n=0.5, Y_0 = W) [26]. The impedance data are given in Table 3.

Figure 4b shows the Bode phase angle plots and figure 4c shows phase angle plots recorded for mild steel electrode immersed in 1 M HCl in the absence and presence of various concentrations of cimetidine at its open circuit potential. The values of Bode impedance magnitude (S) and maximum phase angles (a°) are listed in Table 4.

Table 4. The slopes of the Bode impedance magnitude plots at intermediate frequencies (S) and the maximum phase angles (α) for mild steel in 1 M HCl solution at different (100 mgL^{-1}) concentrations of cimetidine at 308 K

Inhibitors	- S	-α°
Blank	0.502	40.30
100	0.721	69.12
200	0.739	74.65
500	0.755	78.73

In the intermediate frequency region, a linear relationship between log |Z| against log f, with slope near -1 and the phase angle tends to become -90°, can be observed. This response is a characteristic of capacitive behavior. An ideal capacitive response would result in a slope of -1 and a phase angle of -90°; however, it is well known that an electrochemical system generally does not behave in an ideal manner [27]. In our case, in intermediate frequencies region, a linear relationship between log |Z| vs. log f with a slope near -0.76 and the phase angle approaching -80° has been observed. These deviations considered to be the deviation from the ideal capacitive behavior at intermediate frequencies. The Bode phase angle plots show single maximum (one time constant) at intermediate frequencies, broadening of this maximum in presence of cimetidine account for the formation of a protective layer on electrode surface [28].

3.2.2. Potentiodynamic polarization

Polarization curves for mild steel at various concentrations of cimetidine in are shown in Figure 6.

It is clear from the potentiodynamic curves that the presence of cimetidine, in acid solution, decreases the corrosion rate. The decrease in I_{corr} value is due to the adsorption of the inhibitor molecules. It is observed that both the cathodic and anodic reactions are suppressed with the addition of cimetidine which suggests it inhibit both anodic dissolution and cathodic hydrogen evolution reaction. Electrochemical corrosion parameters *i.e.* corrosion potential (E_{corr}), cathodic and corrosion current density (I_{corr}) obtained from the Tafel extrapolation of the polarization curves along with inhibition efficiency are given in Table 5.

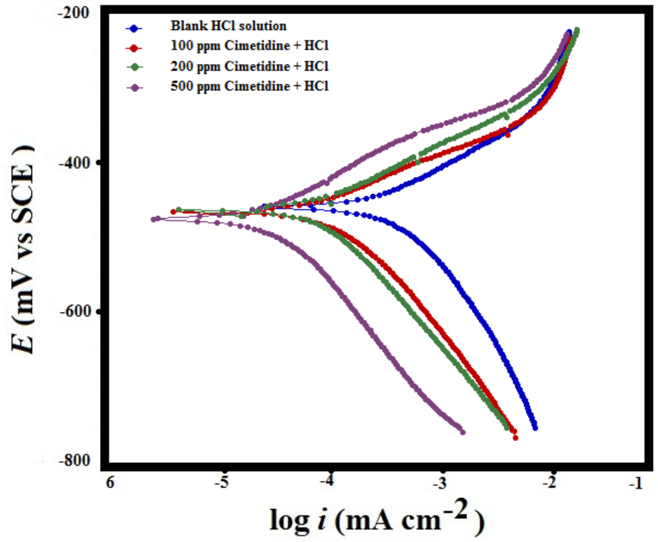

Figure 6. Potentiodynamic polarization curves for mild steel in 1 M HCl in absence and presence of various concentrations of cimetidine at 308 K

Table 5. Electrochemical Impedance Spectroscopy measurements on mild steel electrode in 1 M HCl in absence and presence of different concentration of cimetidine at 308 K

Inhibitor mgL^{-1}	I_{corr} (µA/cm)	E_{corr} (mV/ SCE)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	θ	η (%)
Blank	1540	-446	90.0	121.3	--	--
100	560	-465	57.7	137.7	0.636	63.6
200	271	-469	65.8	127.1	0.824	82.4
500	82	-479	63.4	132.3	0.946	94.6

The inhibition efficiency η % was calculated using the following equation:

$$\eta\% = \frac{I^{0}_{\mathrm{corr}} - I^{\mathrm{i}}_{\mathrm{corr}}}{I^{0}_{\mathrm{corr}}} \times 100 \qquad (11)$$

where, $I°_{corr}$ and I^{i}_{corr} are the corrosion current density in absence and in the presence of cimetidine , respectively. There was no significant change in the E_{corr} values in the presence of cimetidine which suggest that it is mixed type inhibitor [29, 30].

The values of β_c changed significantly with increasing cimetidine concentrations, which indicated the effect of the compound on the kinetics of hydrogen evolution [31]. Compared with the blank, the anodic curves of the working electrode in the acid solution containing cimetidine shifted obviously to the direction of the current reduction, which implied that the cimetidine could also suppress the anodic reaction. Only as the change in E_{corr} value was more than 85 mV, a compound could be recognized as an anodic or a cathodic type inhibitor [32]. The largest displacement of E_{corr} was about 33 mV (Table 5). Therefore, cimetidine might act as a mixed-type inhibitor. Corrosion is an electrochemical phenomenon and inhibitors decrease the velocity of electrochemical electrode reactions. A lower I_{corr} value for cimetidine solutions implies that the rate of electrochemical reactions was reduced due to the formation of a barrier layer over the mild steel surface by the cimetidine molecules [33].

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 are shown in Figure 7. The calculated quantum chemical parameters such as E_{HOMO}, E_{LUMO}, $\Delta E_{LUMO\text{-}HOMO}$, dipole moments ($\mu$) are listed in Table 6. The molecular structure of cimetidine shows that the molecules seems to adsorb on steel surface by sharing of electrons of the nitrogen and oxygen atoms with iron to form coordinated bonds and π-electron interactions of the aromatic rings.

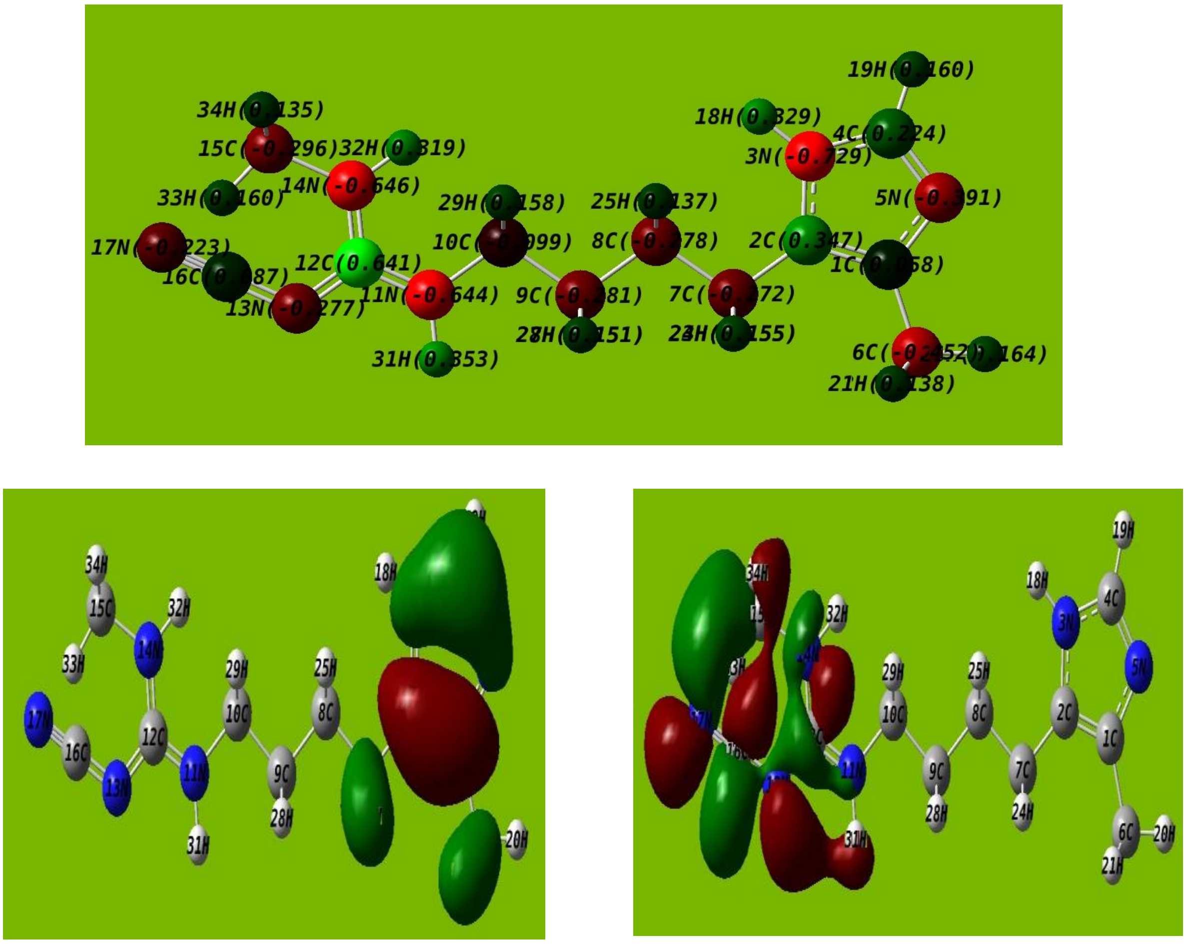

Figure 7. (a) Optimized molecular structure (b) HOMO (c) LUMO molecular orbital density distribution of Cimetidine.

Table 6. Calculated quantum chemical parameters of Cimetidine.

Quantum Parameters	Cimetidine
HOMO (hartree)	-0.20080
LUMO (hartree)	0.02564
ΔELUMO-HOMO (hartree)	0.22644
Dipole Moment (μ)	4.7714

The value of highest occupied molecular orbital, E_{HOMO} indicates the tendency of the molecule to donate electrons through nitrogen and oxygen atoms to acceptor molecule with empty and low energy orbital. E_{LUMO} indicates the tendency of the molecule to accept electrons, with the trend often being that the lower E_{LUMO} is, the greater is the ability of that molecule to accept electrons [34]. The energy gap ΔE is an important parameter that is related to reactivity of the inhibitor molecule towards the metal surface. A high $E_{H\text{-}L}$ is associated with a less tendency towards reactivity while a low $E_{H\text{-}L}$ is an indication of a great tendency towards reactivity [35]. In this case, cimetidine showed a strong tendency towards reactivity. Polarity of a covalent bond (Dipole moment μ) can be understood by distribution of electrons in a molecule and large values of dipole moment μ favour the adsorption of inhibitor.

3.4. Mechanism of inhibition

The Corrosion inhibition of mild steel in hydrochloric acid solution by cimetidine can be explained on the basis of adsorption as depicted in Figure 8.

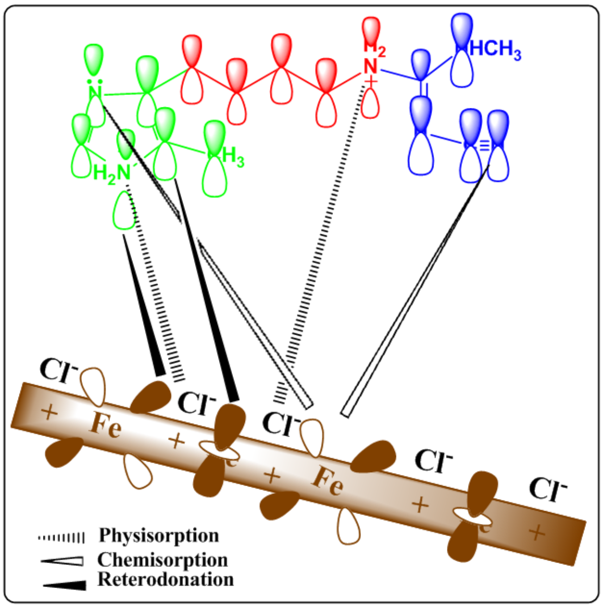

Figure 8. Mechanism of inhibition

Interaction is shown between inhibitor molecules and mild steel surface:

(a) Protonated inhibitor molecules with already adsorbed chloride ions (Physical adsorption)

(b) Interaction of lone pair of electron of N atoms or π electrons of aromatic ring with vacant d-orbitals of the surface Fe atoms (Chemical adsorption).

(c) Interaction of d-electrons of Fe with the high energy orbitals of inhibitor molecules (Reterodonation)

4. CONCLUSIONS

1. The results obtained from different measurements such as weight loss, EIS and polarization measurements showed that cimetidine inhibits corrosion of mild steel in 1 M HCl and these studies gave consistent results.

2. The polarization studies revealed that the inhibitor is of mixed-type.

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

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