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Investigation of Gliclazide Drug as Novel Corrosion Inhibitor for Mild Steel in 1 M HCl Solution

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Inhibition performance of Gliclazide as corrosion inhibitor for mild steel (MS) in 1 M HCl solution was studied by weight loss measurements and electrochemical tests. It showed 91% inhibition efficiency at 400 ppm concentration. Polarization study indicates that Gliclazide behaves as mixed type inhibitor. The adsorption of Gliclazide on mild steel surface follows Langmuir adsorption isotherm. The values of free energy of adsorption (ΔG°_{ads}) indicate that adsorption of Gliclazide is a spontaneous process and it involves both physical and chemisorption.

Keywords: Gliclazide, Mild steel, Weight loss, Electrochemical measurements, Adsorption.

1. INTRODUCTION

Organic inhibitors are widely used to mitigate the excessive loss of metal incurred in many industrial processes such as pickling, acid cleaning, and oil well acidizing[1-2].Numerous organic and non-organic compounds have been studied as inhibitors to protect metals from corrosion attack [3]. The majority of the inhibitors are organic compounds containing heteroatoms, such as oxygen, nitrogen or sulphur, and multiple bonds, through which they are adsorbed on the metal surface [4-8].

The adsorption requires the existence of attractive forces between the adsorbate and the metal [9-10]. There are a wide range of organic inhibitors but unfortunately most of them are expensive and hazardous to health. Thus it remains an important goal to find low cost and eco-friendly inhibitors. In recent years, researchers are paying more emphasis on development of green corrosion inhibitors. Survey of literature reveals that a few pharmaceutically active compounds have been evaluated as effective corrosion inhibitors for different metals [11-16].In continuation of our work on drugs as

corrosion inhibitors we have investigated the inhibition action of Gliclazide drug as corrosion inhibitor on mild steel in 1 M HCl. Gliclazide drug is an oral hypoglycemic (anti-diabetic drugs) and is classified as a sulfonylurea [17].

2. EXPERIMENTAL

2.1. Materials

All the tests were performed on the 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

Gliclazide drug is commercially available as a trade name Diamicron.The compound is in its purest state, having molecular formula ($C_{15}H_{21}N_3O_3S$) and melting point (163-169 $^{\circ}C$). Its chemical structure is shown in Fig. 1. All the concentrations of the inhibitor in acid solution, were taken in ppm (parts per million) by weight.

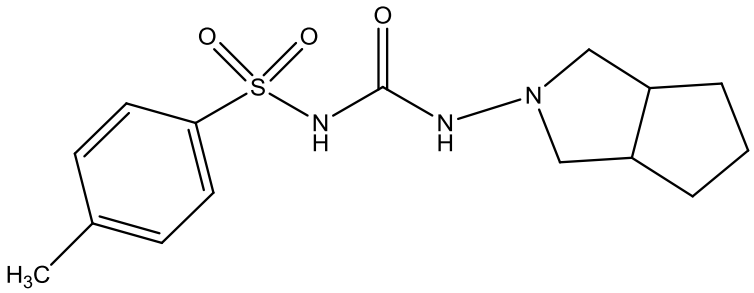

Figure1. Molecular structure of 3-(7-azabicyclo [3.3.0] oct-7-yl)-1-(4-methylphenyl) sulfonyl-urea.

2.3. Weight loss measurements

The MS specimens of rectangular size 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 absence and presence of different concentration of inhibitor. All the test solutions were kept in thermostat. After 3 h, the specimens were taken out, washed, dried and weighed accurately. 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 MS specimens, a total area of one MS specimen, t is the immersion time (3 h) and D is density of MS in (gcm^{-3}). The inhibition efficiency (η%) of inhibitor for the corrosion of MS was calculated as follows,

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

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

2.4. Electrochemical measurements

Three electrochemical techniques, namely potentiodynamic polarization and linear polarization resistance (LPR), and AC-electrochemical impedance spectroscopy (EIS), were used to study the corrosion behavior of mild steel in absence and presence of inhibitor. All experiments were performed in conventional three electrode cell, using electrodes connected to Potentiostat/Galvanostat G300-45050 (Gamry Instruments Inc., USA) Echem Analyst 5.0 software package was used for data fitting. Cell assembly consists of mild steel as working electrode with an exposed area of 1 cm^2, platinum electrode as an auxiliary electrode, and standard calomel electrode (SCE) as reference 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}. Linear Polarization Resistance (LPR) experiments were done from −0.02 V to +0.02 V versus open 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 absence and presence of different concentration of inhibitor.

3. RESULTS AND DISCUSSION

3.1. Electrochemical measurements

3.1.1. Potentiodynamic polarization measurements

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 electrochemical data reveals that the value

of I_{corr} decreases in presence of varying concentration of inhibitor thereby causing inhibition of corrosion. Polarisation curves are shown in Fig. 2. The inhibition efficiencies were calculated from I_{corr} values by using the following equation;

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

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 MS in 1 M HCl in absence and presence of different concentration of Gliclazide

Inhibitor concentration(ppm)	E_{corr} (mVvs SCE)	β_a (mV/dec)	β_c (mV/dec)	I_{corr} (μA cm^2)	η%	R_p (Ω cm^2)	η%
Blank	-448	46	96	1070	-	14.0	-
100	-478	48	81	227	78.7	42.2	66.8
200	-479	65	143	182	82.9	78.2	82.0
300	-480	63	124	125	88.3	94.5	85.1
400	-485	43	66	91	91.4	112.2	87.5

The maximum efficiency 91.4% was obtained at a concentration of 400 ppm. The values of E_{corr} do not shift significantly in presence of inhibitor suggesting that it is mixed type inhibitor [18-19]. The increase in R_p values further confirms the effectiveness of Gliclazide drug as corrosion inhibitor [20].

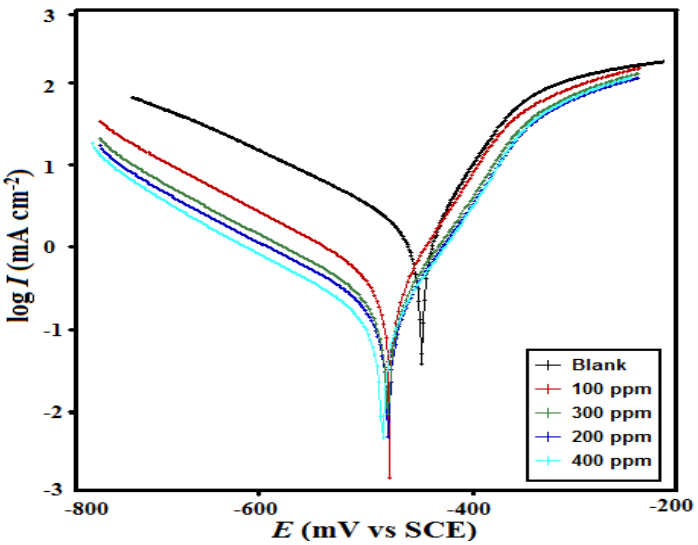

Figure 2. Polarization curves for MS in 1 M HCl in absence and presence of different concentration of inhibitor.

3.1.2. Electrochemical impedance spectroscopy (EIS)

The electrochemical behavior of MS in 1 M HCl in absence and presence of Gliclazide drug was studied by EIS. Nyquist plot, Bode plot and equivalent circuit of mild steel in absence and presence of inhibitor are presented in Fig. 3a-c. The Nyquist plots appeared as depressed semi-circles with one capacitive loop in 1 M HCl solution.The analysis of Nyquist plots reveals that the corrosion process is mainly charge transfer controlled [21]. Equivalent circuit for MS in 1 M HCl has been shown Fig. 3(b). The values of double layer capacitance, C_{dl} was calculated from equation,

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

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 inhibitor

Inhibitor concentration(ppm)	R_{ct} (Ω cm^2)	n	Yo ($10^{-6}\Omega^{-1}$ cm^{-2})	C_{dl} (μF cm^{-2})	η%
Blank	12.1	0.868	242	100.6	-
100	31.5	0.878	126	57.4	61.6
200	56.9	0.868	113	52.8	78.5
300	59.2	0.864	91	40.3	79.5
400	79.0	0.874	82	39.7	84.6

The inhibition efficiency is calculated using charge transfer resistance (R_{ct}) as follows,

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

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 R_{ct} value increases, while the C_{dl} value decreases as the concentration of inhibitor increases [22]. The higher values of R_{ct} are generally attributed to slower rate of corrosion of MS. 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 adsorption of inhibitor molecules on MS surface [23].

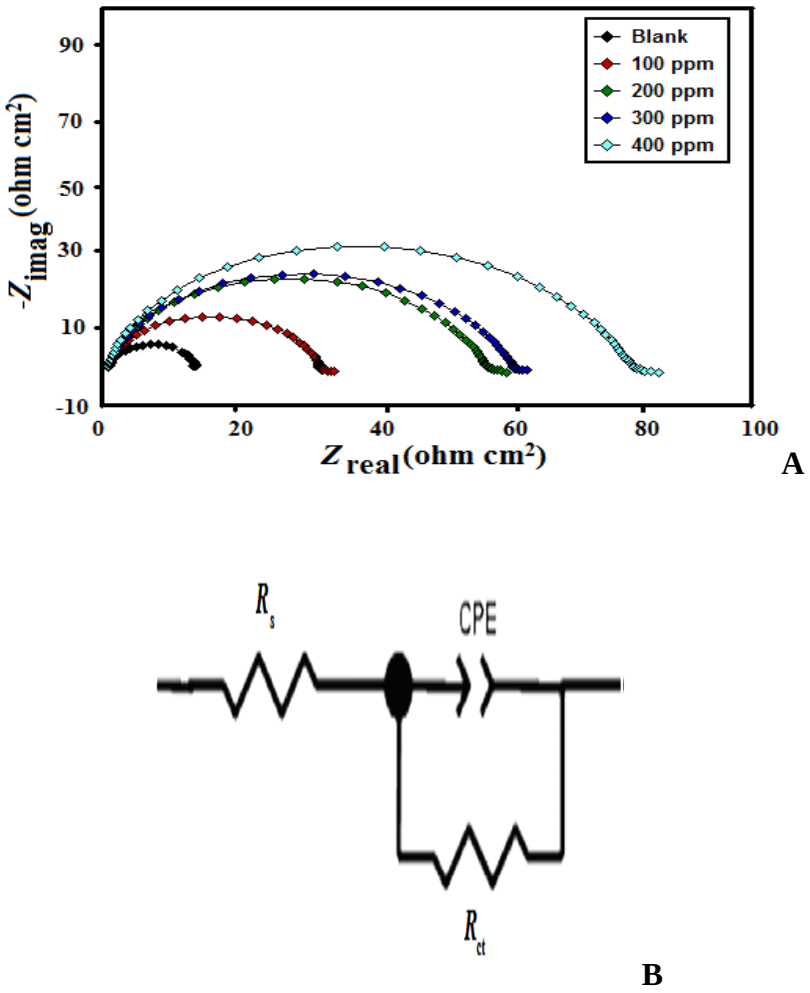

Figure 3. The **(a)** Nyquist plot for MS in 1M HCl and different concentrations of inhibitor used and **(b)** Equivalent circuit used for simulation of data.

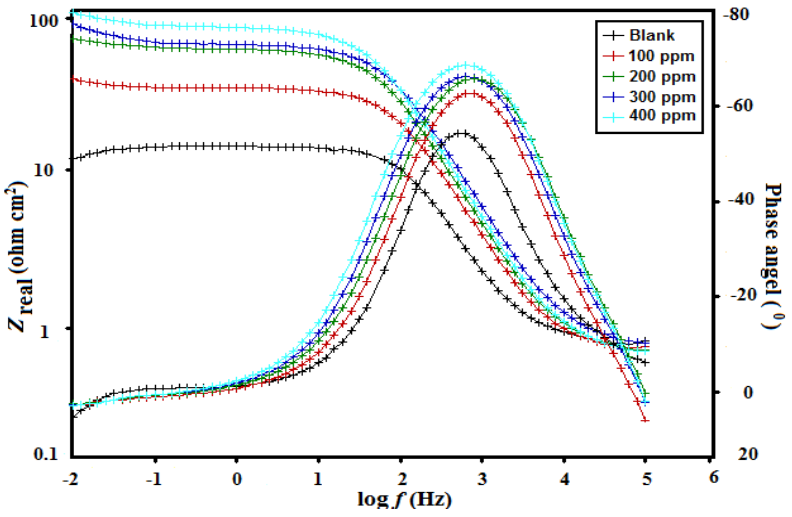

Figure 3(c). Bode-impedance and Phase angle plots for MS in 1 M HCL containing different concentration of inhibitor.

3.2. Weight loss measurements

3.2.1. Effect of inhibitor concentration

The weight loss data obtained for MS in 1 M HCl in presence and absence of different concentration of inhibitor are summarized in Table 3. The corrosion rate values (mg cm^{-2}) of MS in 1 M HCl decreases as the concentration of inhibitor increases [24-25]. The highest inhibition efficiency 86.5% of Gliclazide drug was obtained at 400 ppm.

Table 3. Weight loss data for MS in 1 M HCl at different concentrations of the inhibitor

Inhibitor concentration(ppm)	C_R (mm/y)	Θ	η (%)
Blank	74.2	-	-
100	26.3	0.64	64.5
200	18.9	0.74	74.5
300	15.2	0.79	79.5
400	10.0	0.86	86.5

3.2.2. Effect of temperature

The effect of temperature on inhibition efficiency is shown in Fig. 5.It is clear that inhibition efficiency of Gliclazide decreases from 86% to75% with increasing temperature from 35°C to 65°C indicating that inhibitive film form on the surface is protective in nature up to 65°C. The decrease in inhibition efficiencies might be due to the weakening of adsorbed inhibitor film on the mild steel surface [26].

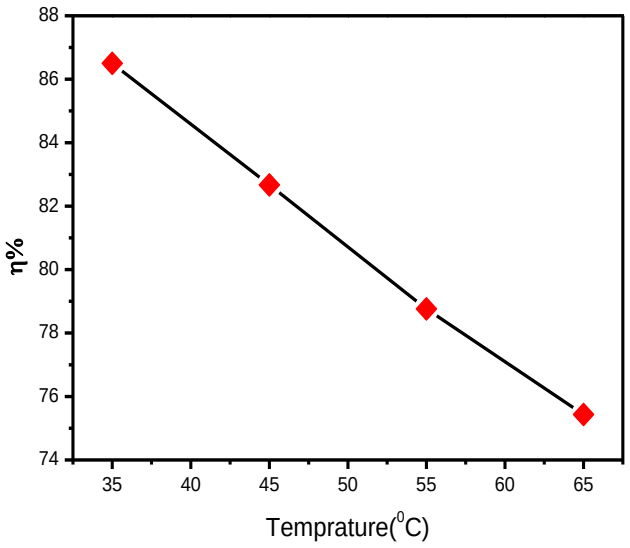

Figure 5. Variation of inhibition efficiency with temperature in 1M HCl on mild steel

3.2.3. Adsorption isotherm

Adsorption parameters give information about the mechanism of corrosion (1 M HCl) and corrosion inhibition (presence of inhibitor in 1 M HCl) due to adsorption. The surface coverage, θ, was calculated according to the following equation,

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

where, C_R and ${}^{inh}C_R$ is the corrosion rate of MS in absence and presence of inhibitor respectively.

Several adsorption isotherms were attempted to fit the degree of surface coverage values (θ) to adsorption isotherms including Frumkin, Temkin, and Langmuir isotherms. The best fit was obtained in the case of Langmuir isotherm which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species [27]. A straight line was obtained on plotting (C/θ) vs θ for Langmuir isotherm with regression coefficient (R^2= 0.9961) confirming this approach as shown in Fig.6,

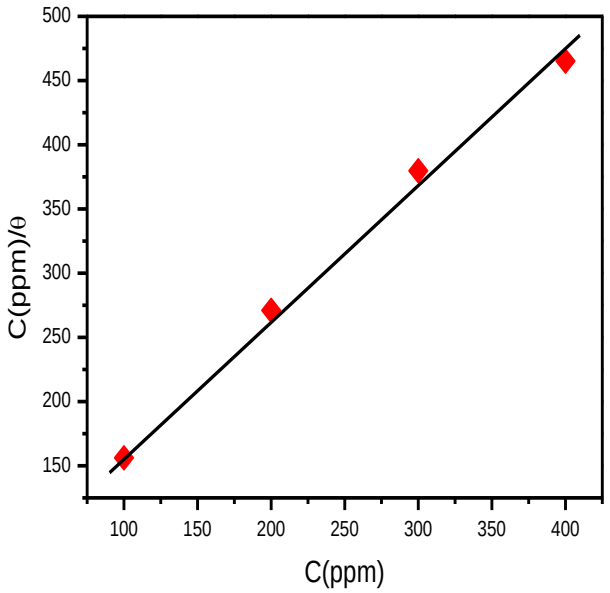

Figure 6. The Langmuir adsorption isotherm plots for MS at different concentrations of inhibitor.

3.2.4. Thermodynamic activation parameters

The activation energy of corrosion process with and without the inhibitor was calculated according to the following equation,

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

where E_a is activation energy for the corrosion of MS in 1 M HCl, R is the gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. A plot of the corrosion rate ln C_R vs 1000/T gives a straight line as shown in Fig. 7(a).The values of E_a in 1 M HCl in absence and presence of Gliclazide are determined from the slope by plotting the values obtained given in Table 4.

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

Inhibitor concentration(ppm)	*E*a (kJmol^{-1})	ΔH^* (kJmol^{-1})	ΔS^* (Jmol^{-1} K^{-1})
Blank	38.15	35.47	-93.62
400	55.52	52.83	-53.74

*E*a in the inhibited solution is higher than that obtained for the free acid solution indicating that the corrosion reaction of MS is inhibited by inhibitor. Higher values of *E*a in the presence of inhibitor can be correlated with increasing thickness of the double layer which enhances the *E*a of the corrosion process [28]. A plot of ln (C_R /T) against 1000/T shown in Fig. 7(b) which give straight lines with a slope of (-ΔH^*/R) and an intercept of [(ln(R/Nh)) + (ΔS^*/R)] to which the values of ΔH^* and ΔS^* are calculated and are given in Table 4.

The ΔH^* (enthalpy of activation) and ΔS^* (entropy of activation) can be calculated by given 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 Plank constant, N is Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. The positive signs of enthalpies (ΔH^*) reflect the endothermic nature of dissolution process. The shift towards positive value of entropies (ΔS^*) shows that the activated complex in the rate determining step represents dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex [29].

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

$$K_{ads} = \frac{\theta}{C(1-\theta)} \quad (9)$$

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5 K_{ads}) \quad (10)$$

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.

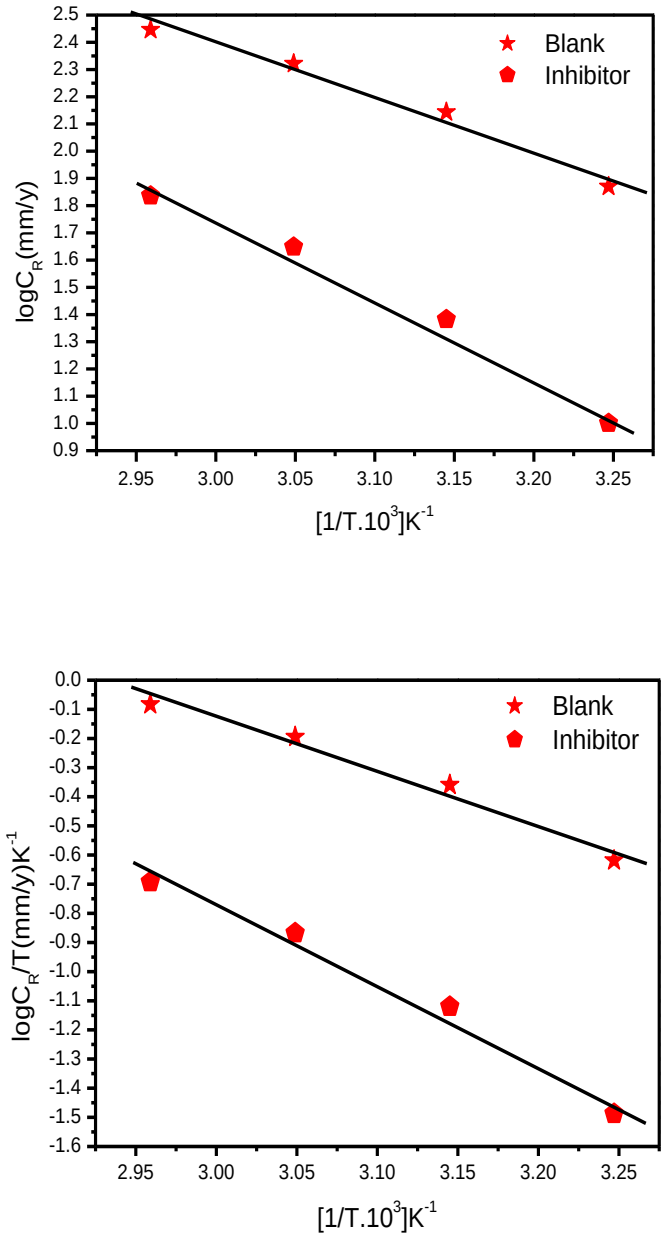

Figure 7. Adsorption isotherm plots (a) log C_R vs. 1000/T (b) log C_R/T vs. 1000/T for MS in 1M HCl in the absence and the presence Gliclazide.

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

Temperature(^{o}C)	$-\Delta G^{o}_{ads}$ (kJ mol^{-1})
35	32.09
45	32.34
55	32.67
65	33.20

The calculated values of ΔG^{o}_{ads} are in the range of -32.09 to-33.20 KJ mol^{-1} indicating that the adsorption of the inhibitor on MS surface involves both physical as well as chemical adsorption [30-31].

3.4. Mechanism of adsorption and inhibition

Corrosion inhibition of metals and alloys is the adsorption of organic inhibitor molecules at the metal/solution interface and the adsorption depends on the molecule's chemical composition, the temperature and the electrochemical potential at the metal/solution interface. The compound inhibits corrosion by controlling both the anodic and cathodic reactions [32]. The adsorption of Gliclazide can be attributed to the presence of polar N atoms and aromatic/heterocyclic rings. Therefore, the possible reaction centres are unshared electron pairs of hetero-atoms and π electrons of aromatic ring [33]. Gliclazide molecules might be protonated in the acid solution as

$$\left[C_{15}H_{21}N_3O_3S\right] + xH^{+} \rightarrow \left[C_{15}H_{21+x}N_3O_3S\right]^{x+} \qquad [11]$$

It is well known that the steel surface bears positive charge in acid solution. The protonated inhibitor molecule could be attached to the mild steel surface by electrostatic interaction between Cl^{-} and protonated Gliclazide. It is impossible for single adsorption mode between inhibitor and metal surface. Gliclazide may adsorb on the metal/acid solution interface by one and/or more of the following ways: (i) electrostatic interaction of protonated molecules with already adsorbed chloride ions, (ii) donor–acceptor interactions between the p-electrons of aromatic ring and vacant d orbital of surface iron atoms, (iii) interaction between unshared electron pairs of hetero-atoms and vacant d-orbital of iron surface atoms [34].

4. CONCLUSIONS

1**.** Gliclazide drug is good inhibitor for MS in 1M HCl. The inhibition efficiency increased with increasing the concentration of the inhibitor with a maximum of 91% observed at 400ppm.

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

3. The adsorption of inhibitor molecules on the MS 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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