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Primaquine: A pharmaceutically active compound as corrosion inhibitor for mild steel in hydrochloric acid solution

I. Ahamad, S. Khan[†], K. R. Ansari and M. A. Quraishi*

Department of Applied Chemistry, Institute of Technology, Banaras Hindu University
Varanasi (India)

ABSTRACT

The corrosion inhibition of mild steel in 1 M HCl by pharmaceutically active compound, the Primaqine (PQ), was investigated by weight loss, electrochemical impedance spectroscopy (EIS) and polarization techniques. Experimental results showed that PQ is an effective inhibitor for the mild steel corrosion in 1 M HCl solutions and it exhibited >90% inhibition efficiency is >90% as low as 0.4 mM inhibitor concentration. Potentiodynamic polarization studies showed that primaquine is a mixed-type inhibitor. The results of EIS showed that PQ inhibits corrosion of mild steel by adsorption mechanism. The adsorption of inhibitor on the mild steel surface followed Langmuir adsorption isotherm. Activation energy (E_a), Gibbs free energy ($\Delta G°_{ads}$), enthalpy (ΔH^*), and entropy (ΔS^*) of corrosion process were calculated and discussed.

Keywords: Corrosion inhibition; Adsorption; Mild Steel; Thermodynamic properties; Drug.

INTRODUCTION

Mild steel is widely used in fabrication of reaction vessels, store tanks, petroleum refineries, and so on [1, 2], but it is severely attacked in acid solutions. Despite continuing advances in development of corrosion-resistant materials, the use of chemical inhibitors often remains the most practical and cost-effective means of preventing corrosion [3, 4]. Organic compounds containing nitrogen, sulfur, oxygen, and heterocyclic compounds with a polar functional group and a conjugated double bond have been reported to inhibit mild steel corrosion [5]. There are a wide range of organic inhibitors but unfortunately most of them are expensive and health hazardous. Thus it remains an important goal to find low cost and ecofriendly inhibitors.

In recent years, the traditional approach on corrosion inhibitors has gradually changed [6]. The researchers are paying more emphasis on development of green corrosion inhibitors [7, 8]. Survey of literature reveals that a few pharmaceutically active compounds have been evaluated as effective corrosion inhibitors for different metals [9-12].

The objective of this paper is to study the inhibitive action of Primaquine (PQ) on corrosion of mild steel in hydrochloric acid solution using weight-loss techniques, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization resistance techniques. The authors have selected PQ as corrosion inhibitor because it is likely to give enhanced inhibition due to presence of lone pair of electrons on hetero-atoms and π-electrons in the PQ molecule. Impedance results were analyzed using an appropriate equivalent circuit with inductive element. The results obtained from the different corrosion evaluation techniques are in good agreement.

EXPERIMENTAL SECTION

Materials

The mild steel used had the following composition (weight %): 0.076 C, 0.012 P, 0.026 Si, 0.192 Mn, 0.050 Cr, 0.135 Cu, 0.023 Al, 0.050 Ni, and the remainder iron. The samples were mechanically abraded with different grades of emery paper (600 to 1200), degreased with acetone, and finally dried at room temperature. The test solution of 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.

Primaquine (PQ) is a commercial name of [N-(6-methoxy quinoline-8Y1) pentane]. It was procured from Ipca Laboratories Ltd. Stock solution of this drug was made by dissolving it directly in 1 M HCl. The structure of the inhibitor is given in Figure 1.

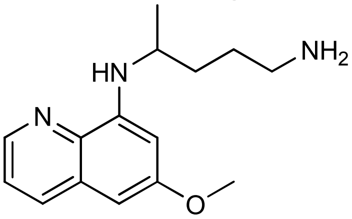


Figure 1: *N*-(6-methoxyquinolin-8-yl)pentane-1,4-diamine

Weight Loss Measurements

Weight-loss measurements were carried out on the mild steel specimens of size 2.5 cm × 2.0 cm × 0.025 cm in 1 M HCl solution with and without addition of different concentrations of PQ. Each sample was weighed by an electronic balance, and then placed in the acid solution. After immersion, the surface of the specimen was cleaned by double distilled water followed by rinsing with acetone, and the sample was weighed again in order to calculate inhibition efficiency (E%) and the corrosion rate (C_R). For each experiment, a freshly prepared solution was used and the solution temperature was thermostatically controlled at a desired value.

Electrochemical measurements

Electrochemical impedance (EIS) measurements and potentiodynamic polarization studies were carried out using a GAMRY PCI 4/300 electrochemical work station based on ESA 400. Gamry applications include EIS 300 (for EIS measurements) and DC 105 software (for corrosion) and Echem Analyst (5.50 V.) software for data fitting. All electrochemical experiments were performed in a Gamry three-electrode electrochemical cell under atmospheric condition with a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The mild steel (8 cm long stem) with the exposed surface of 1 cm^2 was used as working electrode. The experiment was performed as per standard method [13]. EIS measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 100 kHz to 10 mHz with an AC signal amplitude perturbation of 10 mV peak to peak. Potentiodynamic polarization studies were performed with a scan rate of 1 mVs^{-1} in the potential range from 250 mV below the corrosion potential to 250 mV above the corrosion potential. All potentials were recorded with respect to the SCE.

The values of $E\%$ were calculated from weight loss measurement, EIS and polarization measurements, respectively using following equations [14]:

$$E\% = \frac{w_0 - w_i}{w_0} \times 100 \qquad (1)$$

Where w_0 is weight loss in absence of inhibitor and w_i is weight loss in presence of inhibitor.

$$E_{EIS}\% = \frac{R_{t,i} - R_{t,0}}{R_{t,i}} \times 100 \qquad (2)$$

Where $R_{t,0}$ and $R_{t,i}$ are charge transfer resistances in absence and presence of PQ, respectively.

$$E_P\% = \frac{I_{corr,0} - I_{corr,i}}{I_{corr,0}} \times 100 \qquad (3)$$

Where $I_{corr,0}$ and $I_{corr,i}$ are corrosion current densities in absence and presence of PQ, respectively.

RESULT AND DISCUSSION

Weight loss measurements

The corrosion parameters obtained from weight loss measurements for the mild steel in 1 M HCl solution in the absence and presence of different concentrations of PQ are listed in Table 1. It is found that $E\%$ increases and corrosion rate (C_R) decreases with increase in PQ concentration from 0.02 to 0.4 mM. The maximum inhibition efficiency of PQ was 98% at concentration of 0.4 mM.

The effect of temperature on the corrosion inhibition of the mild steel in absence and presence of 0.4 mM PQ in 1 M HCl solution at a temperature range 308 to 338 K is shown in Figure 2. It is seen that inhibition efficiency slightly increases from 98% to 99% with increase in the solution temperature from 308 K to 338 K. The result of this study shows that PQ is a effective inhibitor upto 338 K.

Table 1: Corrosion parameters obtained from weight loss measurements for the mild steel in 1 M HCl containing different concentrations of PMQ after 3 h immersion

Inhibitor concentration (mM)	Weight loss (mg cm^{-2} h^{-1})	E (%)	C_R (mm $year^{-1}$)
Blank	7	–	78
0.02	0.6	91	7
0.04	0.4	94	5
0.1	0.3	95	4
0.2	0.2	97	3
0.4	0.1	98	2

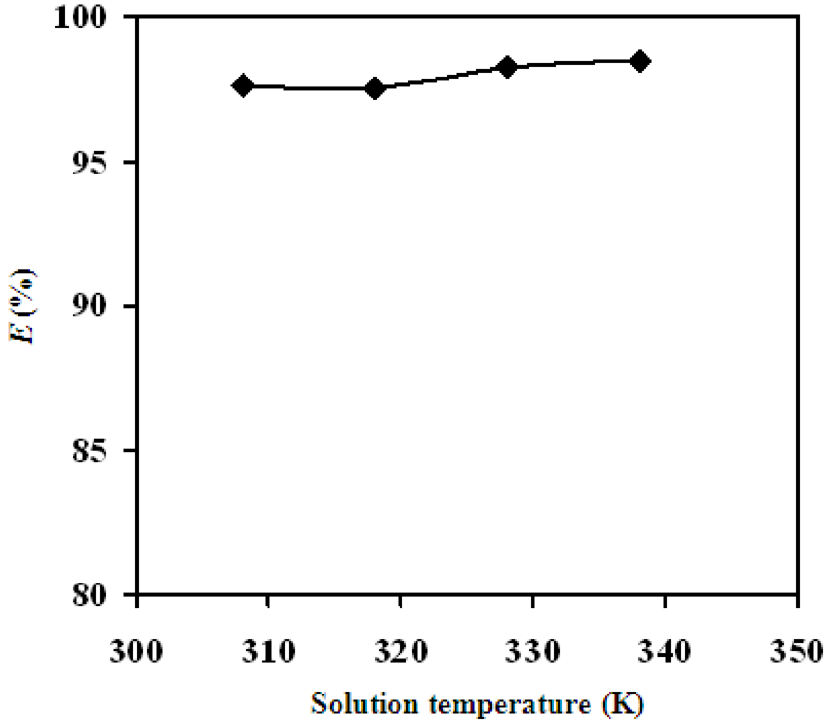


Figure 2: Effect of solution temperature on corrosion resistant properties of mild steel in 1 M HCl in the presence of 0.4 mM PQ.

Thermodynamic activation parameters of inhibition process

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 0.4 mM PQ. It is well known that for iron and steel in acidic solutions, the logarithm of corrosion rate (C_R) can be expressed as a straight line function of the absolute temperature ($1/T$) according to the Arrhenius equation:

$$\log C_R = \log \lambda - \frac{E_a}{2.303RT} \tag{4}$$

where C_R is the corrosion rate, E_a is the activation energy, R is the molar gas constant, T is the absolute temperature. Figure 3a shows plots of log C_R vs. $1/T$ for mild steel corrosion in 1 M HCl in the absence and presence of 0.4 mM PQ. Straight lines were obtained with slope equal to $-E_a = 2.303\ R$. Plots of log (C_R/T) versus $1/T$ for mild steel in 1 M HCl in the absence and presence of 0.4 mM PQ are shown in Figure 3b. The straight lines were obtained according to the transition state equation:

$$C_R = \frac{RT}{Nh}\exp\left(-\frac{\Delta H^*}{RT}\right)\exp\left(\frac{\Delta S^*}{R}\right) \tag{5}$$

where ΔH^* is the entropy of activation, ΔS^* is the enthalpy of activation, h is Planck's constant, and N is Avogadro's number.

The calculated values of activation energy, activation enthalpies, and activation entropies are given in Table 2. These values indicated that the presence of the inhibitor decreases the activation energy, activation enthalpy, and activation entropy for the corrosion process. The decrease in activation energy indicating a strong adsorption of the inhibitor molecules on the mild steel surface signifies that PQ is a powerful inhibitor. Smaller value of E_a in presence of PQ is an indication of 'chemisorption' mode of adsorption. Similar results were reported by Popova et al. [15]. Data in Table 2 further shows that the enthalpy of activation is all positive. The positive sign of the enthalpy reflects the endothermic nature of the mild steel dissolution process. The entropy of activation in the uninhibited and inhibited solutions is negative. The negative value of entropy of activation in the absence and presence of inhibitor implies that the activated complex is the rate-determining step and represents association rather than dissociation, meaning that a decrease in disordering takes place on going from reactants to the activated complex [16].

Adsorption isotherm and free energy of adsorption

The degree of surface coverage values (θ) obtained from three different measurements (viz., weight loss, EIS and Tafel) using the equation ($\theta = E\%/100$) assuming a direct relationship between surface coverage and inhibition efficiency were tested graphically by fitting to different isotherms. Attempts were made to fit θ values to the Freundlich, Temkin, Langmuir, and Flory-Huggins isotherms, and the correlation coefficient (R^2) values were used to determine the best fit isotherm.

The best results were obtained for the Langmuir adsorption isotherm. The characteristics of the Langmuir adsorption isotherm are given by the equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{6}$$

where C_{inh} is inhibitor concentration, K_{ads} is adsorption equilibrium constant for corrosion process. Figure 4 shows the plots of C_{inh}/θ versus C_{inh}. The linear plots were obtained indicating that the experimental data obtained from three different measurements fits the Langmuir adsorption isotherm.

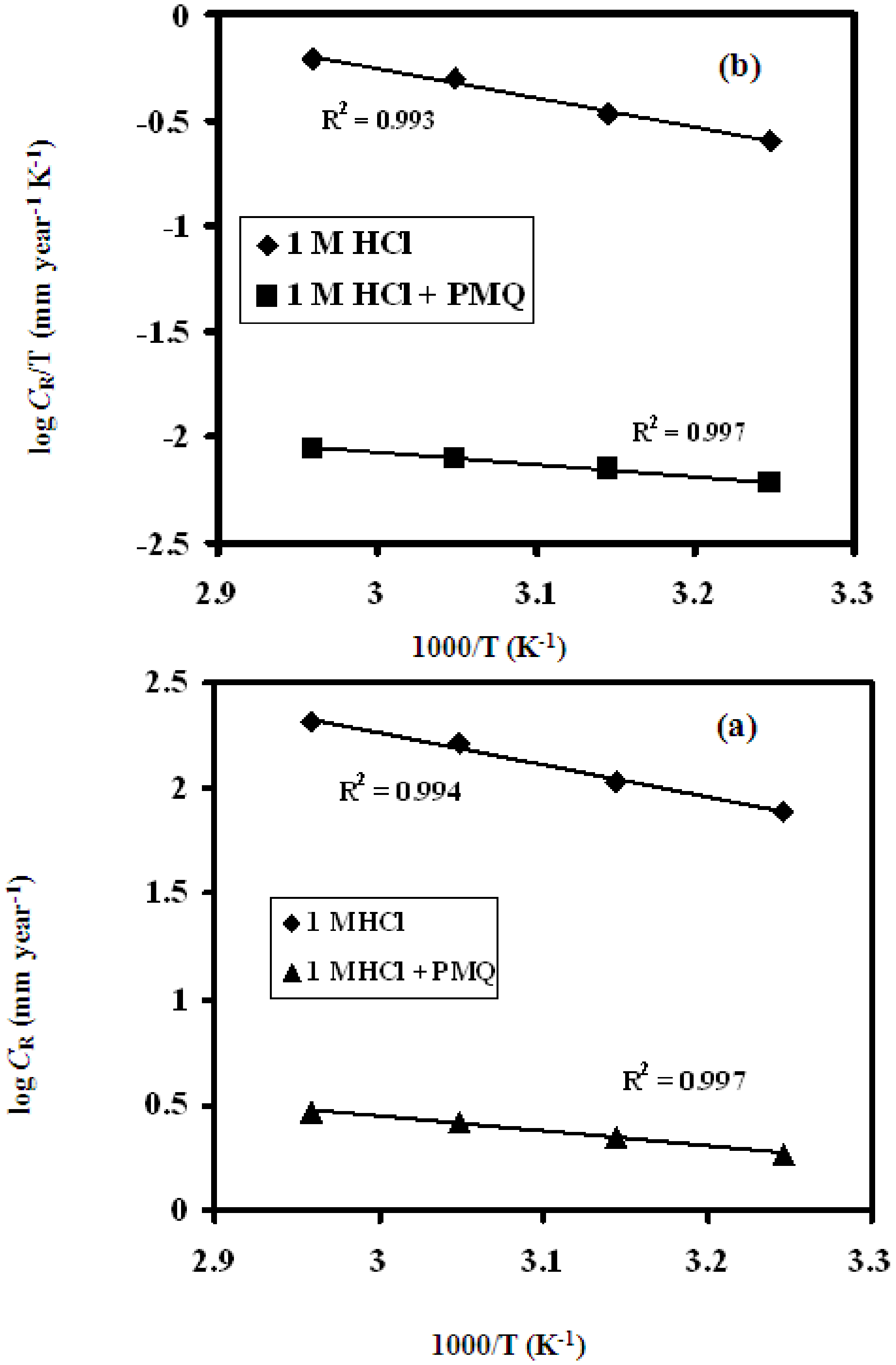


Figure 3: Plots of (a) log C_R vs. 1/T and (b) log (C_R/T) vs. 1/T for mild steel in 1 M HCl solution containing 0.4 mM PQ.

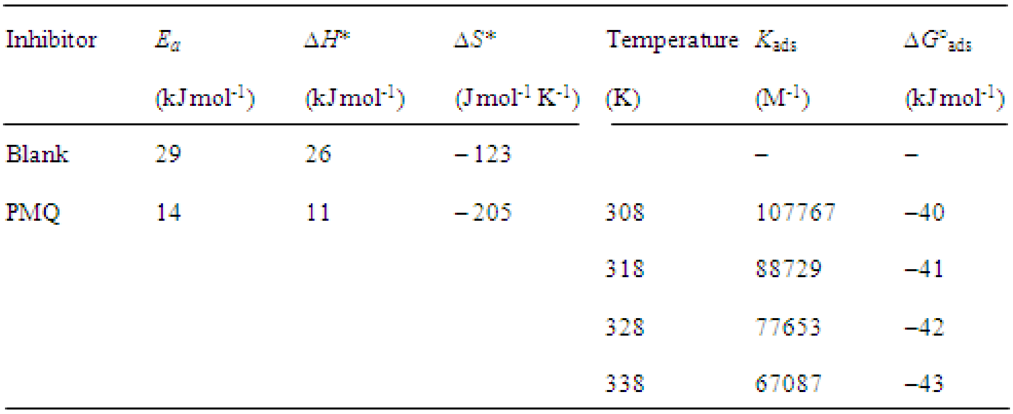
The values of K_{ads} at different temperatures are given in Table 2. The equilibrium constant of adsorption process (K_{ads}) is related to the free energy of adsorption (ΔG°_{ads}) by the equation:

$$K_{\mathrm{ads}} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^{\mathrm{o}}_{\mathrm{ads}}}{RT}\right) \qquad (7)$$

where 55.5 is the concentration of water in mol L^{-1}.

The values of $\Delta G°_{ads}$ were evaluated using Equation (7) for the 0.4 mM PQ at various temperatures and are presented in Table 2. The values of $\Delta G°_{ads}$ indicate the spontaneous adsorption of PQ on the mild steel. Generally, values of $\Delta G°_{ads}$ up to -20 kJ mol^{-1} are consistent with electrostatic interaction between the charged metal and charged molecules, which signifies physical adsorption, while values more negative than -40 kJ mol^{-1} signifies chemical adsorption [17-20]. The value of $\Delta G°_{ads}$ was found to increase from −40 to −43 kJ mol^{-1} with increase in temperature from 308 to 338 K. This indicated that the adsorption of PQ on the mild steel surface is a typical chemisorption. The lower value of activation energy in presence of PQ than in its absence (Table 2) further corroborated the chemical mode of adsorption.

Table 2: Thermodynamic parameters for the mild steel in 1 M HCl in the absence and the presence of 0.4 mM PMQ



Inhibitor	E_a (kJmol^{-1})	ΔH^* (kJmol^{-1})	ΔS^* (Jmol^{-1} K^{-1})	Temperature (K)	K_{ads} (M^{-1})	$\Delta G°_{ads}$ (kJmol^{-1})
Blank	29	26	−123		–	–
PMQ	14	11	−205	308	107767	−40
				318	88729	−41
				328	77653	−42
				338	67087	−43

Electrochemical impedance spectroscopy (EIS) measurements

Figures 5a-b shows Nyquist plots and Bode Z-curves for the mild steel in 1 M HCl in the absence and in presence of different concentrations of PQ. It can be seen that Nyquist plots contain depressed semicircles. Such behavior is the characteristic of solid electrodes and often referred to as frequency dispersion. This frequency dispersion can be attributed to roughness and heterogeneities of the solid surfaces [21].

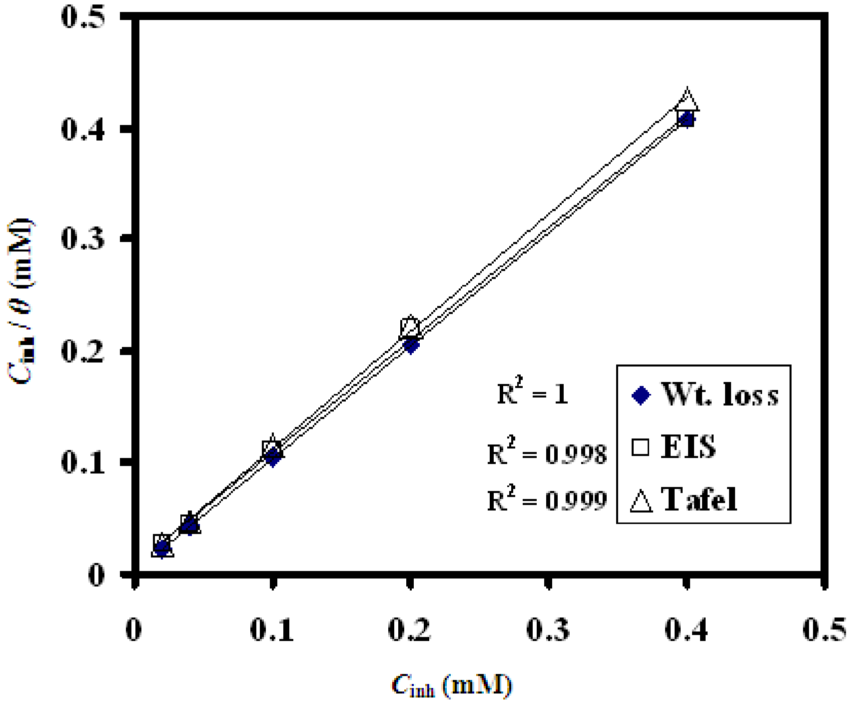
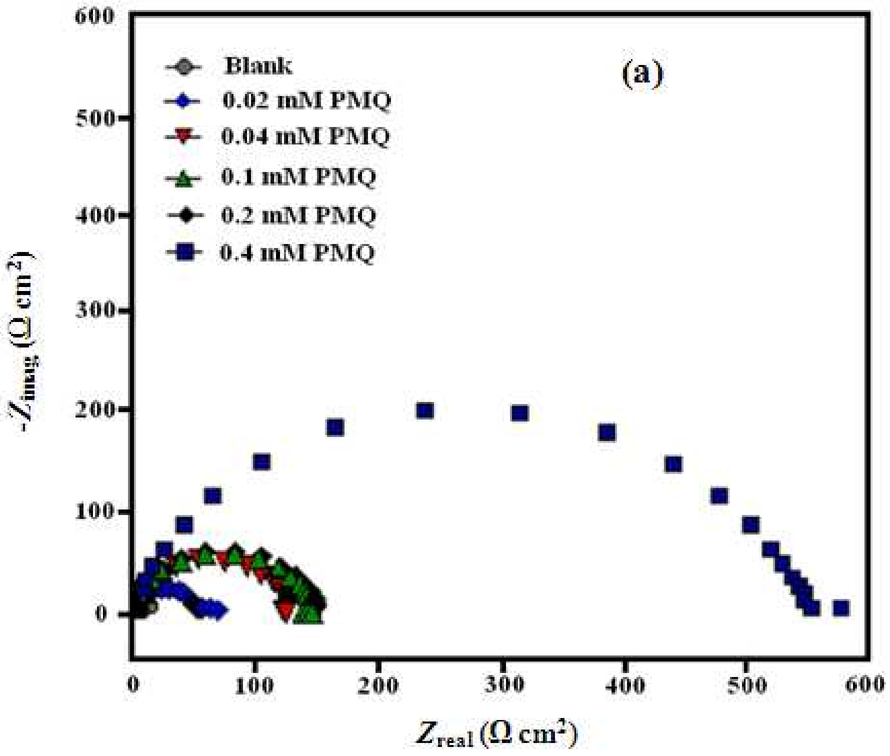
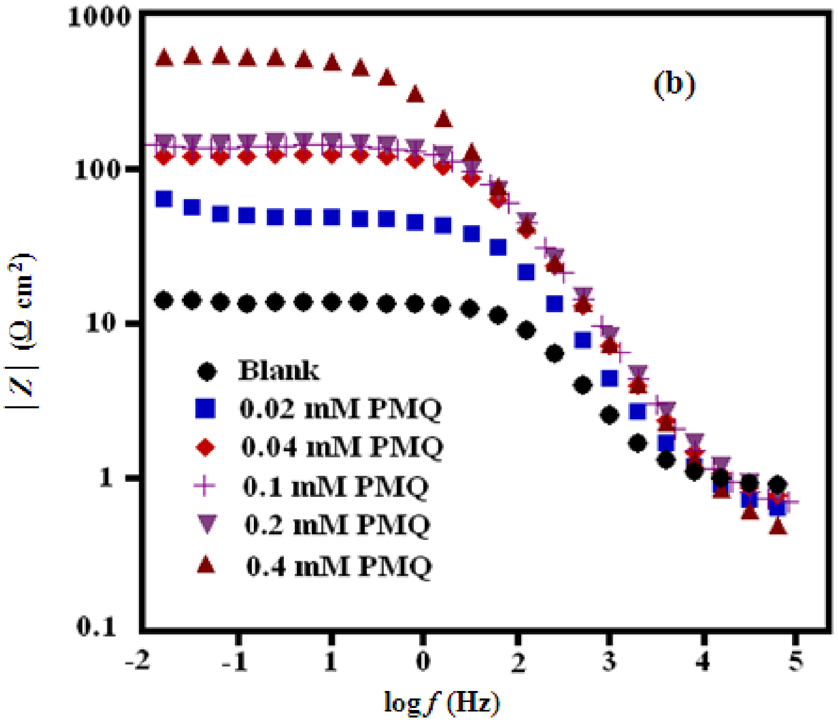
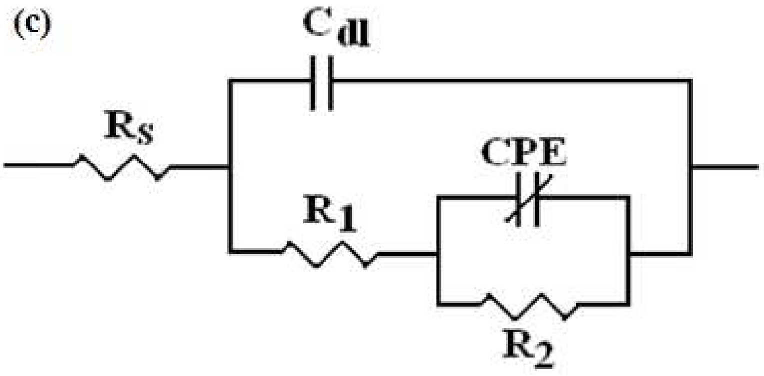


Figure 4: Langmuir adsorption isotherm plots for mild steel in 1 M HCl with different concentrations of PQ by different methods.




(b)
1000
100
10
1
0.1
|Z| (Ω cm²)
-2
-1
1
0
2
3
4
5
log f (Hz)
● Blank
■ 0.02 mM PMQ
◆ 0.04 mM PMQ
+ 0.1 mM PMQ
▼ 0.2 mM PMQ
▲ 0.4 mM PMQ


(c)
Cdl
Rs
CPE
R1
R2

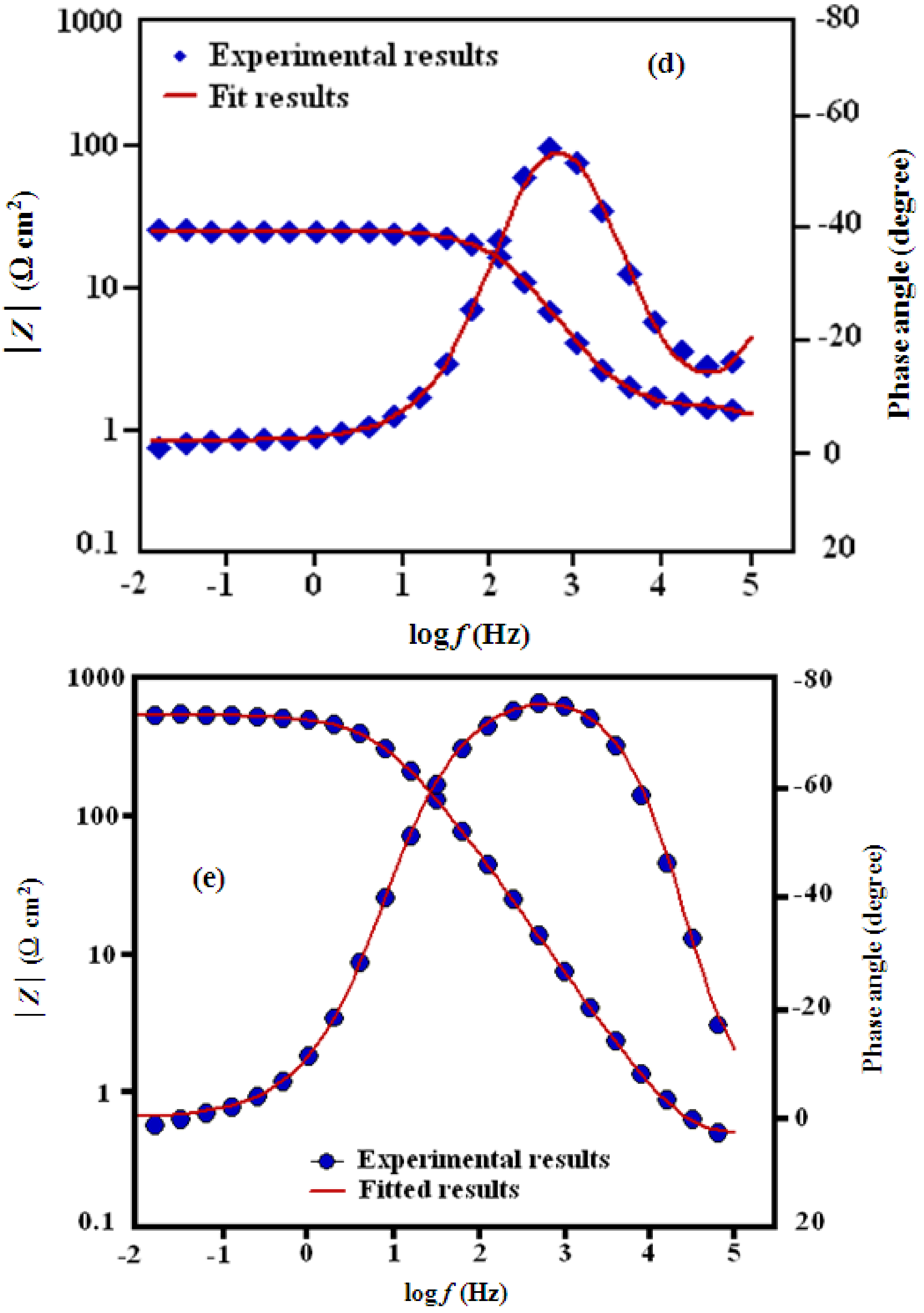


Figure 5: (a) Nyquist plots and (b) Bode Z-curves for mild steel in 1 M HCl solution in absence and presence of different concentrations of PQ; (c) equivalent circuit that models the metal/solution interface; (d) and (e) Bode plots (with fitted results, representative example) for mild steel in 1 M HCl solution and 1 M HCl + 0.4 mM PQ, respectively.

The corroding surface of mild steel in 1 M HCl is inhomogeneous because of its roughness, presence of impurities, dislocations, grain and subgrain morphology, etc. The depression of the capacitance semicircle, whose centre lies under the real axis, confirms this as well.

The distributed capacitance is presented through CPE. The impedance of the CPE is given by:

$$Z_{\mathrm{CPE}} = Y^0 \, (j\omega)^{-\mathrm{n}} \qquad (8)$$

where Y^0 is a proportional factor and n has a meaning of phase shift. It is seen that at

$n = 1$, CPE gives pure capacitance (C) behaviour whose impedance is [15]:

$$Z_{\mathrm{C}} = (j\omega C)^{-1} \qquad (9)$$

In order to fit and analyze the EIS data an equivalent structure model (Figure 5c) was used and the sum of R_1 and R_2 corresponds to charge transfer resistance (R_t) [22]. According to this equivalent circuit, the experimental data were found to be suitably well fitted within the limits of experimental error and reproducibility of data. The reprehensive fitting results using above-mentioned structure model are shown in Figures 5d-e (representative example). The structure parameters calculated accordingly are presented in Table 3. The values of Y^0 can be used for comparison without leading to any significant fault; however, Y^0 should be converted into capacitance (C_{dl}) when experimental data are to be used to determine the parameters of system. Capacitance values can be calculated from CPE parameter values Y^0 and n using the following equation [22]:

$$C_{\mathrm{dl}} = \frac{Y^0 \omega^{\mathrm{n}-1}}{\sin(n\pi/2)} \qquad (10)$$

where $\omega = 2\pi f_{\max}$ ($f_{\max}$ is the frequency at which imaginary component of complex plane plot is maximum). Thus calculated values of C_{dl} were given in Table 3.

Data in Table 3 reveals that R_t value increase with increasing PQ concentration and, however, C_{dl} value decreases much in the presence of PQ. This situation was a result of the adsorption of inhibitor molecules at the metal/solution interface. A decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer can cause decrease in C_{dl} values, suggesting that the inhibitor molecules with low dielectric constant replace the water molecules with high dielectric constant. From impedance measurements one can conclude that the inhibitor efficiency increases with increasing PQ concentration.

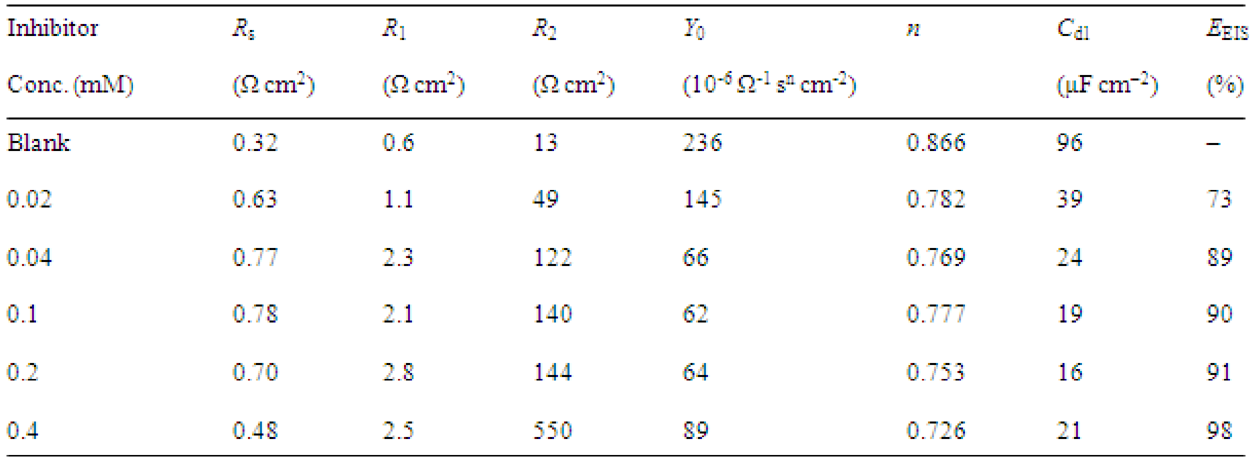
Polarization measurements

Figure 6 shows the polarization curves of mild steel in 1 M HCl in the absence and presence of various concentrations of PQ. Various corrosion parameters obtained from Tafel fit by selecting polarization curves 50 mV in both anodic and cathodic direction from E_{corr} value were presented in Table 4. The polarization of the mild steel in 1 M HCl solution containing inhibitor shows that the presence of PQ decreases the corrosion current density (I_{corr}). The decrease in I_{corr} value could be attributed to the inhibitor adsorption on surface of mild steel and adsorption process enhances with increasing inhibitor concentration.

Data in Table 4 show that E_{corr} value did not change in a regular manner in the presence of different concentrations of PQ and E_{corr} value shows a little change, indicating that PQ acts as a mixed-type inhibitor (Ahamad and Quraishi, 2010). The values of Tafel slope constants (b_a and b_c) remain more or less constant in the presence of inhibitor suggesting that the effect of inhibitor is not as large as to change the mechanism of corrosion. Thus inhibition of the mild steel corrosion in one molar hydrochloric acid solution is merely blocking of surface active sites due to adsorption of PQ molecules.

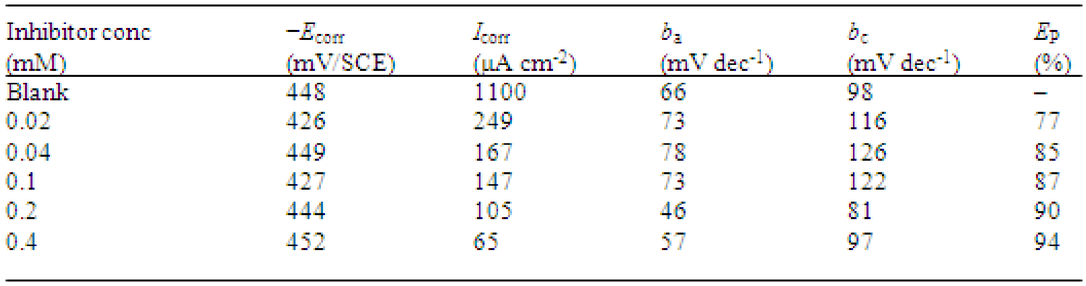
Results obtained from different methods (viz., weight loss, EIS, and polarization curves measurements) were consistent and inhibition of mild steel corrosion in 1 M HCl solution increases with increase in the concentration of PQ.

Table 3: Electrochemical parameters for the mild steel in 1 M HCl in the absence and the presence of PMQ at different concentrations



Inhibitor Conc. (mM)	R_s (Ω cm^2)	R_1 (Ω cm^2)	R_2 (Ω cm^2)	Y_0 ($10^{-6}\ \Omega^{-1}$ s^n cm^{-2})	n	C_{dl} (μF cm^{-2})	E_{EIS} (%)
Blank	0.32	0.6	13	236	0.866	96	–
0.02	0.63	1.1	49	145	0.782	39	73
0.04	0.77	2.3	122	66	0.769	24	89
0.1	0.78	2.1	140	62	0.777	19	90
0.2	0.70	2.8	144	64	0.753	16	91
0.4	0.48	2.5	550	89	0.726	21	98

Table 4: Polarization parameters and corresponding inhibition efficiency for corrosion of the mild steel in 1 M HCl containing different concentrations of PMQ



Inhibitor conc (mM)	$-E_{corr}$ (mV/SCE)	I_{corr} (μA cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	E_P (%)
Blank	448	1100	66	98	–
0.02	426	249	73	116	77
0.04	449	167	78	126	85
0.1	427	147	73	122	87
0.2	444	105	46	81	90
0.4	452	65	57	97	94

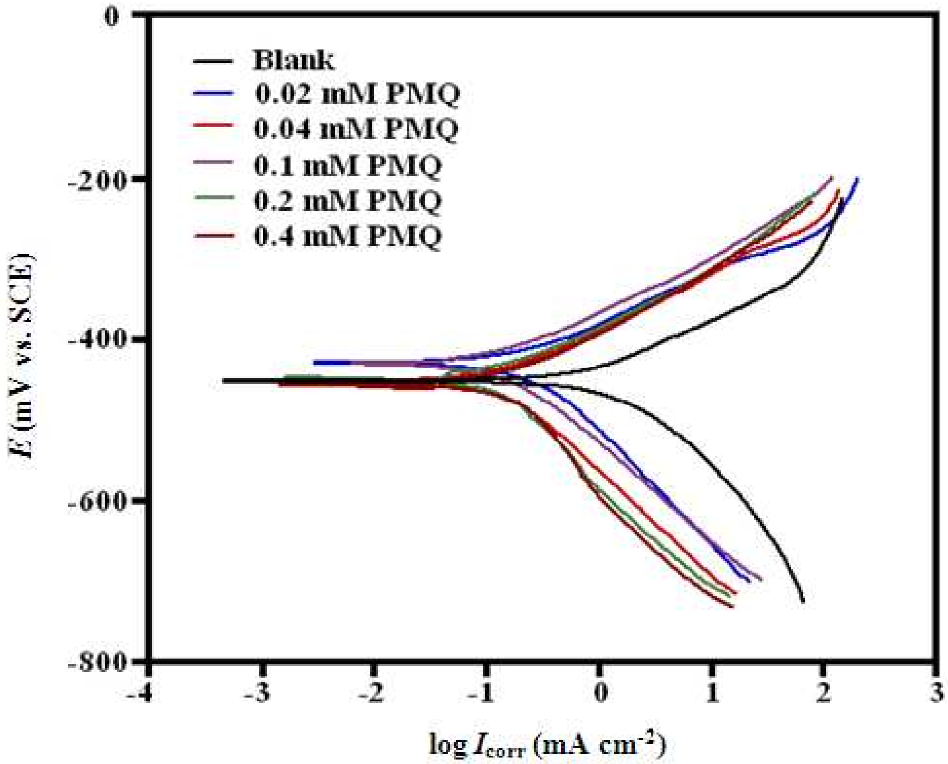


Figure 6: Tafel curves for mild steel in 1 M HCl in absence and presence of different concentrations of PQ.

Mechanism of corrosion inhibition

The results shows that investigated primaquine inhibit the corrosion of mild steel in 1 M HCl through its adsorption at the metal/solution interface. A skeletal representation of the proposed mode of adsorption is shown in Figure 7 and clearly indicates the active adsorption center. The adsorption of PQ at the mild steel surface can take place through its active centres; unshared electron pairs of hetero-atoms and pi-electron of the quinoline moiety. So that mode of adsorption depends on the affinity of the metal towards the p-electron clouds of the molecule. Metals such as Fe and Cu, which have a greater affinity towards aromatic moieties, were found to adsorb aromatic rings in a flat orientation.

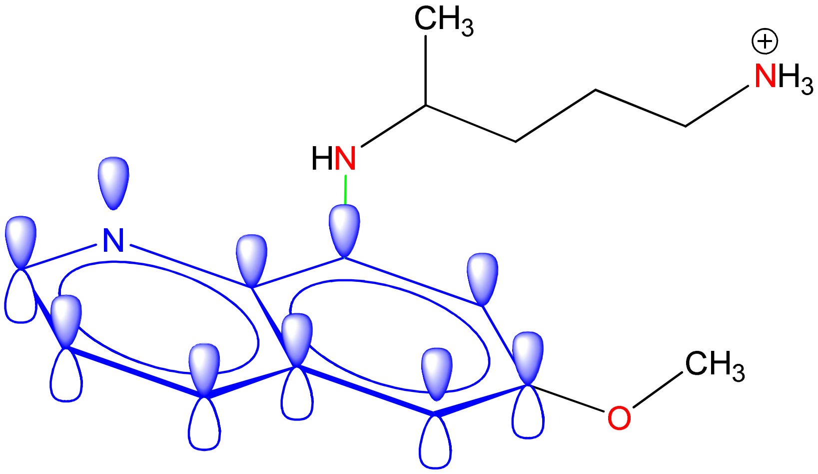


Figure 7: Skeletal representation of the adsorption mode of PQ.

In acid solution inhibition of metallic corrosion occurs through (i) electrostatic interaction of protonated molecules with already adsorbed chloride ions, (ii) donor-acceptor interactions between the π-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. For adsorption of organic compounds at the metal/solution interface, generally two modes are considered. In one mode, the neutral molecules adsorbed on the surface of mild steel via the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the hetero atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor–acceptor interactions between π-electrons of the aromatic ring and vacant d-orbitals of surface iron atoms. In second mode, since it is well known that the steel surface bears positive charge in acid solution, so it is difficult for the protonated inhibitor molecules to approach the positively charged mild steel surface (H_3O^+/metal interface) due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, thus they could bring excess negative charges in the vicinity of the interface and favour more adsorption of the positively charged inhibitor molecules, the protonated molecules can adsorb on the metal surface through electrostatic interactions. Good inhibition efficiency exhibited by PQ can be attributed to the presence of hetero-atoms (N and O), methoxy group, and quinoline moiety [23].

CONCLUSION

1. The results obtained from different measurements such as weight loss, EIS and polarization measurements showed that primaquine inhibits corrosion of mild steel in 1 M HCl and these studies gave consistent results.
2. Tafel curves showed that PQ is a mixed type inhibitor.
3. EIS results were interpreted using an equivalent circuit in which a capacitance is in parallel to the series resistors R_1 and R_2 and a CPE in parallel to R_2 was used in order to give more accurate fit to the experimental results.
4. Adsorption of PQ on the mild steel surface obeyed the Langmuir adsorption model with standard free energies of adsorption (ΔG°_{ads}) ranging in between -40 kJ mol^{-1} and -43 kJ mol^{-1} which could be attributed to high adsorption of PQ on the mild steel surface, forming a strong protective film.
5. Adsorption of PQ on the mild steel surface was a typical chemisorption.

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