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Electrochemical investigation of 6-methylquinoxaline-2,3(1H,4H)-dione as potential corrosion inhibitor for carbon steel in hydrochloric acid solution

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ABSTRACT

The inhibition performances of 6-methylquinoxaline-2,3(1H,4H)-dione (MQD) on carbon steel corrosion in hydrochloric acid solution was studied the using electrochemical impedance spectroscopy (EIS) and Tafel polarization techniques. The effects of inhibitor concentration on the inhibition efficiency have been studied. Inhibition efficiency increased with increase in concentration of this compound within the concentration range 10^{-6} - 10^{-3} M. Changes in impedance parameters (charge transfer resistance, R_{ct} , and double layer capacitance, C_{dl}) were indicative of adsorption of quinoxaline derivative on the carbon steel surface, leading to the formation of protective films. The adsorption of this inhibitor takes place according to Langmuir's adsorption isotherm. Potentiodynamic studies revealed that the inhibitor is of cathodic type. The results obtained from the EIS studies showed good agreement with the results from potentiodynamic polarization techniques.

Keywords: Quinoxaline derivative, Carbon steel, HCl, EIS, Polarization.

INTRODUCTION

The corrosion of steel is a fundamental academic and industrial concern that has received a considerable amount of attention [1]. Acid solutions are widely used in industry. Some of the important fields of application being acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. In acidic media, the use of hydrochloric acid in pickling of metals, acidization of oil wells and in cleaning of scales is more economical, efficient and trouble-free compared to other mineral acids [2]. Thus the use of corrosion inhibitors is one of the most practical methods for corrosion protection of steel especially in acidic media [3-5]. Organic compounds containing electronegative functional groups and π -electrons in triple or conjugated double bonds are usually good corrosion inhibitors. Heteroatoms such as sulphur, phosphorus, nitrogen and oxygen as well as aromatic rings in their structure are the major adsorption centers. The compounds used as corrosion inhibitors act through a process of surface adsorption. The efficiency of inhibitors depends on the characteristics of the environment in which it acts the nature of the metal surface and electrochemical potential at the interface. The structure of the inhibitor itself, which includes the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface also have effect on the efficiency of inhibitors [6-30].

The aim of this paper therefore is to further explore the use of quinoxaline derivative as an acid corrosion inhibitor for carbon steel surface in hydrochloric acid solution using electrochemical measurements. The effect of temperature and molecular structure on the inhibition efficiency was also discussed. Figure 1 shows the molecular structure of the quinoxaline derivative utilised in this investigation.

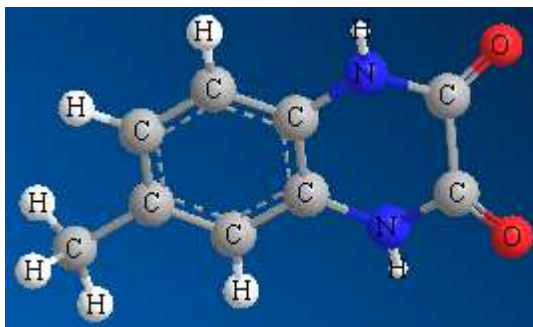


Figure 1. Structure of 6-methylquinoxaline-2,3(1H,4H)-dione (MQD).

MATERIALS AND METHODS

Materials

The steel used in this study is a carbon steel (CS) (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe).

Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. The concentration range of 6-methylquinoxaline-2,3(1H,4H)-dione (MQD) used was 10^{-6} M to 10^{-3} M.

Polarization measurements

Electrochemical impedance spectroscopy

The electrochemical measurements were carried out using Volta lab (Tacussel-Radiometer PGZ 100) potentiostat and controlled by Tacussel corrosion analysis software model (Voltmaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode of surface area of 1 cm^2 . The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp} , the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 303 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit

0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x -axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation [31]:

$$\eta_z \% = \frac{R_{ct}^i - R_{ct}^\circ}{R_{ct}^i} \times 100 \quad (1)$$

where, R_{ct}° and R_{ct}^i are the charge transfer resistance in absence and in presence of inhibitor, respectively.

Potentiodynamic polarization

The electrochemical behaviour of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1.0 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -

900 to -100 mV versus corrosion potential at a scan rate of 1 mV s⁻¹. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). From the polarization curves obtained, the corrosion current (I_{corr}) was calculated by curve fitting using the equation:

$$I = I_{corr} \left[\exp\left(\frac{2.3\Delta E}{\beta_a}\right) - \exp\left(\frac{2.3\Delta E}{\beta_c}\right) \right] \quad (2)$$

The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$\eta_{Tafel} \% = \frac{I_{corr}^{\circ} - I_{corr}^i}{I_{corr}^{\circ}} \times 100 \quad (3)$$

where, I_{corr}° and I_{corr}^i are the corrosion current density in absence and presence of inhibitor, respectively.

RESULTS AND DISCUSSION

Tafel polarization

Effect of inhibitor concentration

Fig. 2 shows the Tafel polarization curves for carbon steel in 1.0 M HCl with the addition of various concentrations of quinoxaline derivative. The important corrosion parameters derived from these curves are presented in Table 1. From Table 1 it is clear that the corrosion current density (I_{corr}) value decreases from 1070 to 30 $\mu\text{A cm}^2$ with the addition of optimum concentration of MQD. However, a shift of corrosion potential (E_{corr}) towards cathodic side *i.e.* -496 to -586 mV was established. Furthermore, depending on the concentration of MQD, a shifting in the E_{corr} (vs. SCE) values to the negative direction and a decrease in cathodic of Tafel slopes has been observed (Table 1). This observation is an indication to that the MQD inhibitor acts as cathodic inhibitor. The classification of a compound as an anodic or cathodic inhibitor is feasible when the corrosion potential displacement is at least 85mV in relation to that one measured for the blank solution [32]. The cathodic polarization curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and the addition of 6-methylquinoxaline-2,3(1H,4H)-dione does not modify the mechanism of this process [33-36].

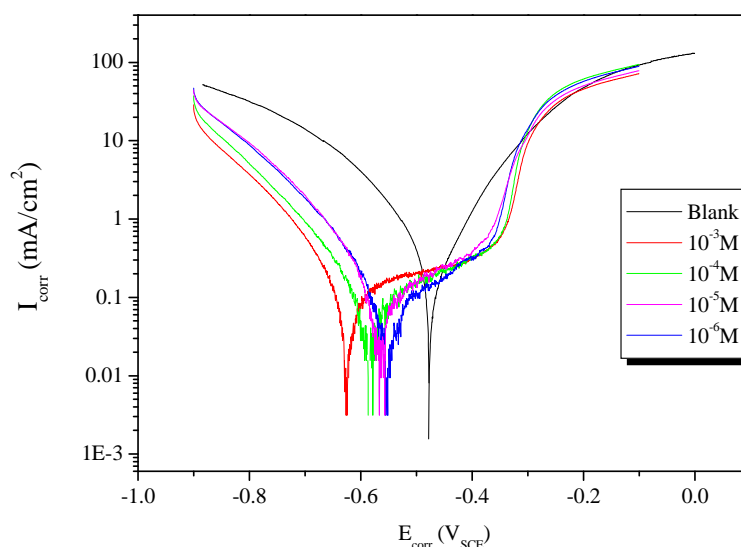


Figure 2. Typical polarization curves for carbon steel in 1.0 M HCl for various concentrations of MQD at 303 K.

Table 1. Potentiodynamic electrochemical parameters for the corrosion of carbon steel in 1.0 M HCl solution in the absence and presence of the investigated inhibitor at 303 K.

Inhibitor	Conc (M)	$-E_{\text{corr}}$ (mV _{SCE})	$-\beta_c$ (mV/dec)	I_{corr} ($\mu\text{A cm}^{-2}$)	η_{Tafel} (%)
Blank	1.0	475	175	1070	-----
MQD	10^{-3}	626	135	30	97.2
	10^{-4}	586	141	50	95.3
	10^{-5}	554	138	55	94.9
	10^{-6}	570	139	85	92.0

EIS measurements

Electrochemical impedance measurements were carried over the frequency range from 100 kHz to 0.01 Hz at open circuit potential. The simple equivalent Randle circuit for these studies is shown in Fig. 4, where R_s represents the solution resistance; the parallel combination of resistor, R_{ct} and capacitor C_{dl} represents the protective film/ metal interface. The impedance behavior of carbon steel in 1.0 HCl with and without addition of various concentrations of this inhibitor is presented as complex impedance plot (Nyquist plot) in Fig. 3. The existence of single semi circle shows the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. Deviation from perfect circular shape is often referred to the frequency dispersion of interfacial impedance. This anomalous behavior is generally attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena [37-39]. It is seen that addition of inhibitor increases the values of charge transfer resistance (R_{ct}) and reduces the double layer capacitance (C_{dl}). The decrease in C_{dl} is attributed to increase in thickness of electronic double layer [40]. The increase in R_{ct} value is ascribed to the formation of protective film on the metal/solution interface [41]. These observations suggest that quinoxaline molecules function by adsorption at metal surface thereby causing the decrease in C_{dl} values and increase in R_{ct} values.

The charge transfer resistance (R_{ct}) and the interfacial double layer capacitance (C_{dl}) derived from these curves are given in Table 2.

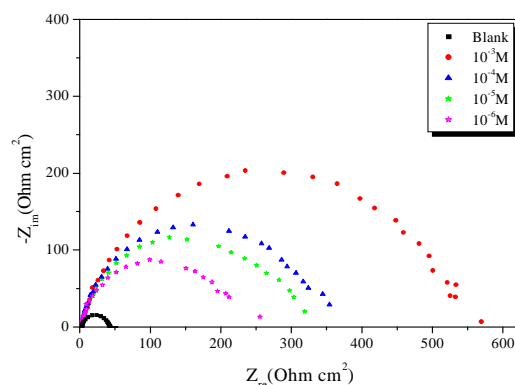
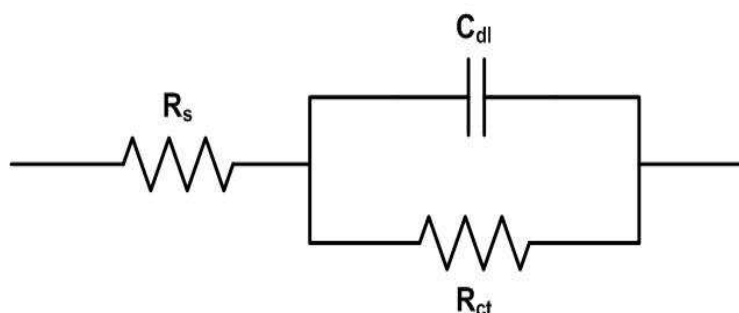
**Figure 3. Nyquist plots of carbon steel in 1.0 M HCl with different concentrations of MQD.****Figure 4. Electrical equivalent circuit (R_s , solution resistance; R_{ct} , charge transfer resistance; C_{dl} , double layer capacitance).**

Table 2. Electrochemical impedance parameters and inhibition efficiency for carbon steel in 1.0 M HCl solution with MQD at 303K.

	Conc (M)	R _{ct} (Ω cm ²)	f _{max} (Hz)	C _{dl} (μF/cm ²)	η _i (%)
Blank	1.0	40.03	40.00	99.38	-----
MQD	10 ⁻³	541.3	4.00	73.54	92.6
	10 ⁻⁴	350.9	5.00	90.75	88.6
	10 ⁻⁵	292.9	6.33	85.88	86.3
	10 ⁻⁶	220.2	6.33	114.24	81.8

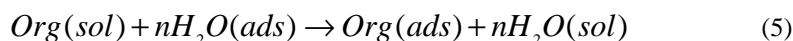
The thickness of the protective layer is related to C_{dl} by the following equation [42]:

$$d_{org} = \frac{\epsilon_0 \epsilon_r}{C_{dl}} \times S \quad (4)$$

where ϵ_0 is the vacuum dielectric constant, ϵ_r is the local dielectric constant, d_{org} is the thickness of the double layer, and S is the surface area of the electrode. This decrease in the C_{dl} may result from a reduction in local dielectric constant and/or an increment in the thickness of the electrical double layer. The phenomenon proposed that quinoxaline molecules function by adsorption at the metal/solution interface. Thus, the change in C_{dl} values was due to the gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface, decreasing the magnitude of metal dissolution [43].

Adsorption considerations

The adsorption process of inhibitor is a displacement reaction where the adsorbed water molecule is being removed from the surface of metal [44]:



$Org(sol)$ and $Org(ads)$ are the organic molecules in the aqueous solution that adsorbed to the metal surface. While $H_2O(ads)$ is the water molecule on the metal surface in which n is the coefficient that represent water molecules replaced by a unit of quinoxaline derivative. To obtain an effective adsorption of an inhibitor on metal surface, the interaction force between metal and inhibitor must be greater than the interaction force of metal and water molecule [45]. The corrosion adsorption processes can be understood using adsorption isotherms. In order to obtain the isotherm, coverage θ as a function of MQD concentration must be obtained. Coverage can be obtained from polarization measurement by the following equation:

$$\theta = \frac{R_{ct}^i - R_{ct}^o}{R_{ct}^i} \quad (6)$$

Langmuir adsorption isotherm is attributing to physisorption or chemisorption phenomenon while Temkin adsorption isotherm gives an explanation about the heterogeneity formed on the metal surface. Chemisorption is attributed to Temkin isotherm [46]. Here, Langmuir, Frumkin and Temkin adsorption isotherm were applied in order to explain the adsorption process of MQD on the carbon steel surface:

$$\text{Langmuir: } \frac{C}{\theta} = \frac{1}{K} + C \quad (7)$$

$$\text{Frumkin: } \ln\left(\frac{\theta}{C(1-\theta)}\right) = \ln K + g\theta \quad (8)$$

$$\text{Temkin: } \ln k + \ln K = g\theta \quad (9)$$

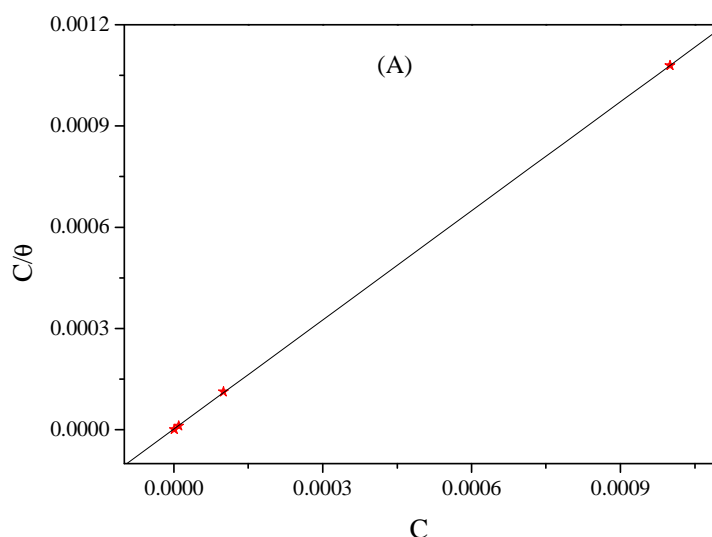
θ is the surface coverage, K is the adsorption-desorption equilibrium constant, C is the concentration of inhibitor and g is the adsorbate parameter. Again, the weight loss measurements were employed in this experiment with the concentration range 10⁻⁶, 10⁻⁵, 10⁻⁴ and 10⁻³ M at 303 K. The corresponding plots are shown in Fig. 5, where the R² value for Langmuir isotherm (Fig. 5A) was 0.99999, Frumkin isotherm (Fig. 5B) was 0.99119 and Temkin isotherm

(Fig. 5C) was 0.99323. From this observation, it is concluded that Langmuir isotherm shows the best correlation with the experimental data. In addition, this also explains the monolayer formation of the inhibitor onto the mild steel surface [44, 47]. The free energy of adsorption ΔG_{ads}° , also can be calculated using the following equation:

$$\Delta G_{ads}^{\circ} = -RTL \ln(55.5K_{ads}) \quad (10)$$

where 55.5 is the molar concentration of water, R is the universal gas constant and T is the temperature in K. The calculated value of free energy of adsorption was found to be $\Delta G_{ads}^{\circ} = -43.31 \text{ kJ mol}^{-1}$, where adsorption-desorption equilibrium constant K value was obtained from the linear regression of Langmuir isotherm (528008.19 M^{-1}).

The negative value of ΔG_{ads}° indicates that the inhibitor, in this case quinoxaline derivative is spontaneously adsorbed onto the carbon steel surface. It is well known that values of ΔG_{ads}° around -20 kJ mol^{-1} or lower are associated with the physisorption phenomenon where the electrostatic interaction assemble between the charged molecule and the charged metal, while those around -40 kJ mol^{-1} or higher are associated with the chemisorption phenomenon where the sharing or transfer of organic molecules charge with the metal surface occurs [48, 49]. The value of the inhibitor was found $43.31 \text{ kJ mol}^{-1}$. This value suggests that quinoxaline derivative molecules adsorbed on the metal surface by chemical process.



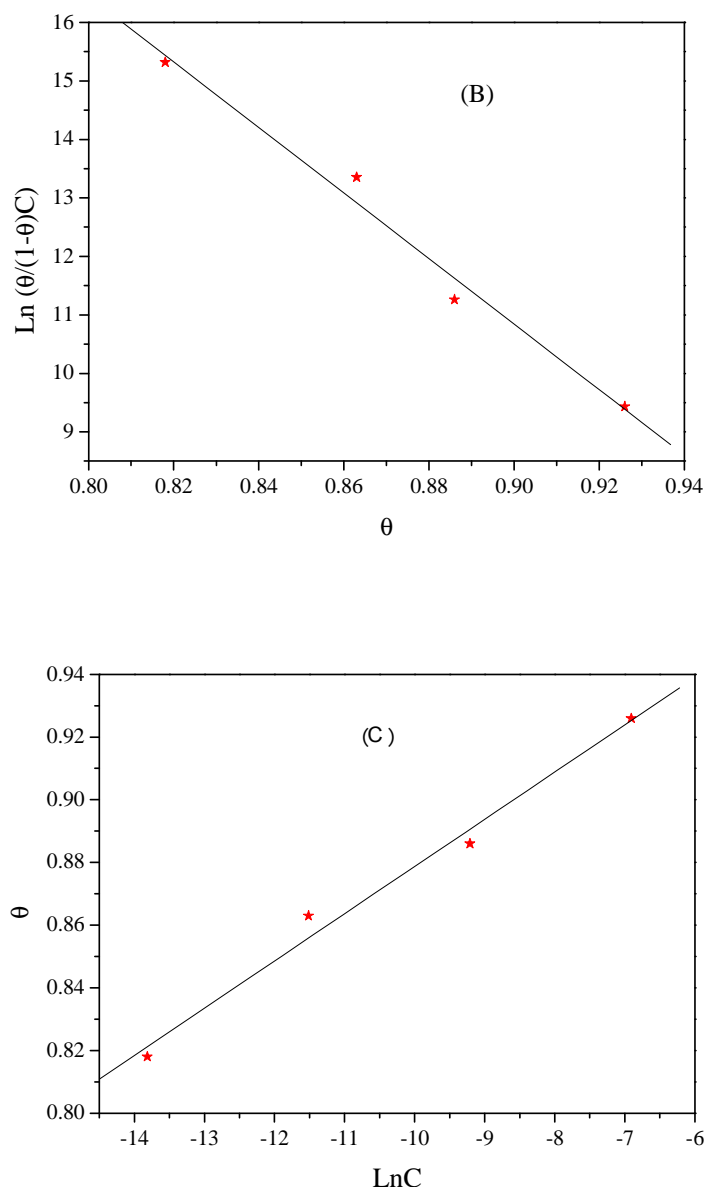
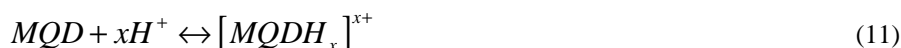


Figure 5. (A) Langmuir, (B) Frumkin and (C) Temkin isotherm for the adsorption of MQD on the surface of carbon steel in 1.0 M HCl.

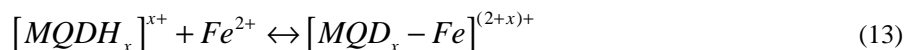
Explanation for adsorption and inhibition

From the experimental results obtained, the inhibition effect of quinoxaline derivative herein referred to as (MQD) in 1.0 M HCl solution can be explained as follows:



Thus, in aqueous acidic solutions, the MQD molecules exist either as neutral molecules or in the form of cations (protonated MQD). Generally, two modes of adsorption could be considered. The neutral MQD molecules may be adsorbed on the metal surface via the chemisorption mechanism involving the displacement of water molecules from the metal surface and the sharing of electrons between nitrogen, oxygen atom and iron. The MQD molecules can be adsorbed also on the metal surface on the basis of donor-acceptor interactions between π -electrons of the heterocycle and vacant d-orbitals of iron. On the other hand, it is well known that the steel surface carries positive charges in acid solution [50], so it is difficult for the protonated MQD molecules to approach the positively charged steel surface (H_3O^+ /metal interface) due to the electrostatic repulsion. Since chloride ions have a smaller degree of

hydration, being specifically adsorbed, they create an excess negative charge towards the solution and favour more adsorption of the cations [41]. The protonated MQD molecules may adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface, i.e. there may be synergism between Cl^- and protonated MQD molecules. Thus, the metal complexes of Fe^{2+} and MQD molecules or protonated MQD molecules might be formed as follows:



CONCLUSION

6-methylquinoxaline-2,3(1H,4H)-dione acts as a good inhibitor for the corrosion of carbon steel in 1.0 M HCl. The inhibition efficiency of quinoxaline derivative increase with inhibitor concentration. The adsorption of quinoxaline derivative follows Langmuir's adsorption isotherm. Potentiodynamic polarization curves reveals that MQD is a cathodic inhibitor. The results obtained from different experimental studies are in good agreement.

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