

# Corrosion Inhibition Behaviour and Adsorption Characteristics of Quinoxaline Derived on Mild Steel C38 E in Acid Medium

H. El Attari<sup>1\*</sup>, S. Mengouch<sup>1</sup>, M. Siniti<sup>2</sup>, L. Khamliche<sup>3</sup>, A. El kihel<sup>4</sup>, H. Ait Sir<sup>4</sup>,  
A. kheribech<sup>5</sup>

Professor, Department of Chemistry, Laboratory de Chimie de Coordination et d'Analytique, Faculty of Science,  
University of Chouaib Doukkali, 24 000 El Jadida, Morocco<sup>1</sup>

Research student, Department of Chemistry, Laboratory de Chimie de Coordination et d'Analytique, Faculty of  
Science, University of Chouaib Doukkali, 24 000 El Jadida, Morocco<sup>1</sup>

Professor, Department of Chemistry, Equipe de Thermodynamique, Surfaces et Catalyse, Faculty of Science,  
University of Chouaib Doukkali, 24 000 El Jadida, Morocco<sup>2</sup>

Professor, Department of Chemistry, laboratory de chimie bio-organiques, Faculty of Science, University of Chouaib  
Doukkali, 24 000 El Jadida, Morocco<sup>3</sup>

Professor, Department of Chemistry, Laboratoire de Chimie BioOrganique, Faculty of Science, University of Chouaib  
Doukkali, 24 000 El Jadida, Morocco<sup>4</sup>

Professor, Department of Chemistry, Laboratory de l'Eau et de l'Environnement, Faculty of Science, University of  
Chouaib Doukkali, 24 000 El Jadida, Morocco<sup>5</sup>

**ABSTRACT:** The inhibition effect of 1,4-dihydroquinoxaline-2,3-dione (DHQD) on the corrosion behavior of Mild Steel C38 E in 1M HCl. solutions was investigated by using potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The results indicate that DHQD is a good inhibitor for the samples under investigation in 1M HCl. solutions. In addition, the inhibition efficiency  $\omega\%$  increases with the inhibitor concentration while decreases with the increasing temperature referring to physical adsorption. The potentiodynamic polarization carried out in 1 M HCl in the absence and presence of the inhibitor clearly proves the fact that this compound behaves as a mixed inhibitor. The adsorption of this compound on the mild steel surface obeys Langmuir's adsorption isotherm. Thermodynamic parameters such as  $E_a$ ,  $\Delta G^{\circ}_{ads}$ ,  $\Delta S^{\circ}_{ads}$ ,  $\Delta H^{\circ}_{ads}$  were calculated to investigate mechanism of inhibition. The inhibition of mild steel in HCl was found to obey Langmuir and thermodynamic-kinetic El-Awady adsorption isotherms. Quantum chemical calculations were employed to give further insight into the mechanism of inhibition action of DHQD.

**KEYWORDS:** 1, 4-dihydroquinoxaline-2, 3-Dione; Corrosion inhibit, carbon steel; Acid inhibition, Electrochemical impedance spectroscopy.

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

## I. INTRODUCTION

Metal and alloys is widely used in industrial operations and the study of the corrosion and inhibition of steel is a subject of practical significance. In order to improve the corrosion protection numerous advanced treatments, including organic compounds have been proposed [1-8]. The reaction of corrosion inhibitors at the metal-solution interface has been evaluated by adsorption characteristics and by investigating the thermodynamics of adsorption. In general it was accepted that the inhibition mechanism is preceded by the formation of an intermediate Fe-adsorbed inhibitor, which is slow at low concentration, and then in a second stage at higher concentration, the formation of a compact inhibitor over-layer on the metal surface [9-14]. It is claimed that if organic molecules have groups like -OH, CO, -CHO -NH<sub>2</sub>, -COOH, -CN, and -SCN, double or triple bonds or unpaired electrons have been proved to perform as very good inhibitors for the corrosion of metals in acidic solution [15-20]. The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface, which consists of the replacement of water molecules at the corroding interface; modifies thus the electrical double layer and forms a protective film that acts a physical barrier blocking the diffusion of ions and the active corrosion sites anodic and/or cathodic [21-26]. In the present study, the effect of 1,4-dihydroquinoxaline-2,3-dione (DHQD) has been investigated for examining its efficacy as an inhibitor for the corrosion of mild steel in acidic solution hydrochloric using three different techniques: weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. It was found that (DHQD) adsorbs on the steel surface according Langmuir and thermodynamic-kinetic El-Awady adsorption isotherms. Adsorption enthalpy were determined and discussed. Effect of temperature was also investigated and activation parameters were evaluated.

## II. EXPERIMENTAL PROCEDURES

### II.1. Mass Loss Measurements

Carbon steel samples with the following composition: 0.38 per cent (C), 0.23 per cent (Si), 0.68 per cent (Mn), 0.01 per cent (P), 0.02 per cent (S) and the remainder iron, were used in the studies. The samples were polished with emery papers from grade 120 to 1200, washed with distilled water, cleaned with acetone, and dried. After being weighed accurately by a balance with high sensitivity the specimens were immersed in 30 mL 1 M HCl with and without various concentrations of the studied inhibitor at different temperatures. After 6 h of immersion, the specimens were taken out, rinsed thoroughly with distilled water, dried and weighed accurately again. Then the tests were repeated at different temperature immersion time. In order to get good reproducibility, experiments were carried out in duplicate. The corrosion rate ( $V_{corr}$ ) was calculated from the following equation:

$$V_{corr} = \frac{M_1 - M_2}{S \cdot t} \quad (1)$$

Where  $M_1$  is the initial weight before immersion,  $M_2$  the final weight after the corrosion test A the geometrical surface area (4 cm<sup>2</sup>), and the period of corrosion test (6 h). The inhibition efficiency  $\omega$  (%) has assessed using a known relation [27]:

$$\omega(\%) = \frac{V_{corr}^0 - V_{corr}^{inh}}{V_{corr}^0} \times 100 \quad (2)$$

Where  $V_{corr}^0$  and  $V_{corr}^{inh}$  are the values of corrosion rate without and with inhibitor, respectively.

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

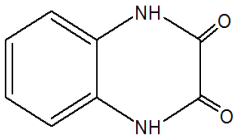
THE STRUCTURAL FORMULA	DESIGNATION AND ABBREVIATION
	<p>quinoxaline-2,3(1H,4H)-dione</p> <p>DHQD</p>

Table 1: Name and structure of the organic compound.

## II.2. Electrochemical measurements

The Electrochemical experiments were carried out in the conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) the working electrode (WE) which was in the form of a square embedded in PVC holder using epoxy resin so that the flat surface was the only surface in the electrode. The working surface area was 1.0 x 1.0 cm<sup>2</sup>, and prepared as described above (Section Weight loss determination). Used material is EC-Lab SP 200 Research Grad model potentiostat/galvanostat/FRA. Data were analyzed using an EC-Lab V10.40 software. The polarization curves were recorded by using three-electrode system. The working electrode was first immersed into the test solution for 30 minutes to establish a steady state open circuit potential ( $E_{ocp}$ ). After measuring the open circuit potential, potentiodynamic polarization curves were obtained with a scan rate of 1 mV/s in the potential range between  $\pm 10$  V relative to the  $E_{ocp}$ . Corrosion current densities values were obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. Inhibition efficiency (% IE) is defined as:

$$\omega(\%) = \frac{i_{corr}^0 - i_{corr}^{inh}}{i_{corr}^0} \times 100 \quad (3)$$

Where  $i_{corr}^0$  and  $i_{corr}^{inh}$  represent corrosion current density values without and with inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) experiments were performed at potential open circuit in the frequency range from 100 kHz to a 10 mHz, with a signal amplitude perturbation of 10 mV. Inhibition efficiency  $\omega(\%)$  is estimated using the following relation:

$$\omega(\%) = \frac{R_{ct}^{inh} - R_{ct}^0}{R_{ct}^{inh}} \times 100 \quad (4)$$

Where  $R_{ct}^0$  and  $R_{ct}^{inh}$  are charge transfer resistance in the absence and presence of the inhibitor, respectively.

## III. RESULTS AND DISCUSSION

### III.1. Electrochemical Measurements

#### III.1.1 Potentiodynamic Polarization

Figure.1 depicts the representative Tafel plots of the corrosion inhibition studies on mild steel with different concentrations of DHQD. The electrochemical parameters of current density ( $i_{corr}$ ), corrosion potential ( $E_{corr}$ ), corrosion rate ( $C_R$ ), cathodic ( $\beta_c$ ) and anodic ( $\beta_a$ ) Tafel constants were calculated from the dc curves and are presented in Table 2 in the absence of an inhibitor, a high current density appeared at 407,915mV, showing a corrosion rate around 345,37  $\mu A.cm^{-2}$  for mild steel C38 E in 1M HCl. DHQD at  $1,5 \cdot 10^{-3}$  M/L, decreased

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

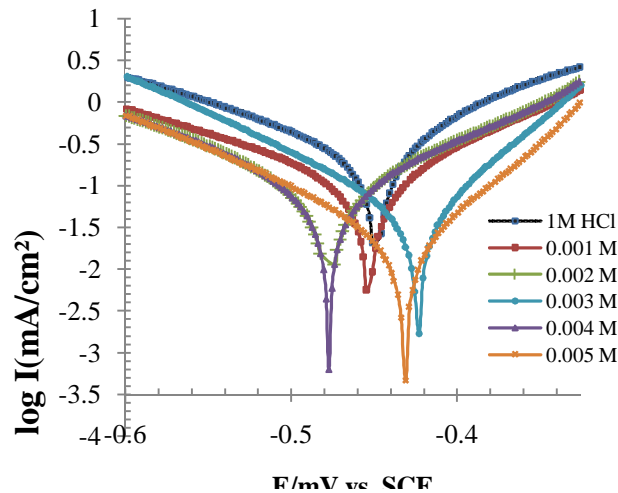


Figure 1: Potentiodynamic polarization curves for carbon steel in 1 M HCl in the absence and presence of different concentrations of DHQD at 298 K

corrosion current densities. In all cases,  $i_{corr}$  decreased at higher inhibitor concentration. The inhibited anodic Tafel slopes were lower in all cases, thus showing the effect of the inhibitor on the iron dissolution reaction. The cathodic Tafel slopes gradually decreased with inhibitor concentration. This alters both ( $\beta_a$ ) and ( $\beta_c$ ) values suggesting that the inhibitor reduces anodic dissolution and retard hydrogen evolution as well indicating the mixed nature of the inhibitor.

of DHQD where as more pronounced change occurs in the values of  $\beta_a$ , indicating that both anodic and cathodic reactions are effected but the effect on the anodic reactions is more prominent. Thus, DHQD acted as mixed type, but predominantly anodic inhibitor [28]. The values of corrosion current densities in the absence ( $i_{corr}^0$ ) and presence of the

Table 2. Electrochemical parameters of steel samples after immersion in 1 HCl in The absence and presence of DHQD at various concentrations.

Conc (M)	$E_{corr}$ (mV/SCE)	$I_{corr}$ ( $\mu A.cm^{-2}$ )	$\beta_a$ (mV/dec <sup>-1</sup> )	$\beta_c$ (mV/dec <sup>-1</sup> )	$\omega(\%)$
Blank	-407,915	354,37	170,8	174,0	
0,001	-447,562	99,27	116,1	154,2	72%
0,002	-467,964	85,71	114,5	145,8	73%
0,003	-401,969	73,76	57,6	142,6	79%
0,004	-459,858	52,03	84,2	142,1	85%
0,005	-413,843	21,27	53,0	123,1	93%

inhibitor ( $i_{corr}^{inh}$ ) were used to estimate the inhibition efficiency from polarization. Increase in inhibition efficiencies with increasing concentration of DHQD reveals that inhibition action is due to adsorption on steel surface and the adsorption is known to depend on the chemical structure of the inhibitor.

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

### III.1.2. Electrochemical impedance spectroscopy (EIS)

The effect of inhibitor concentration on the impedance behavior of mild steel in 1 M HCl solution at room temperature after 6 h immersion time is presented in Figure 3. It was concluded from these plots that the impedance response of carbon steel in 1 M HCl had significantly altered after the addition of inhibitors into the test solutions. These diagrams have similar shape throughout all tested concentrations, indicating that almost no

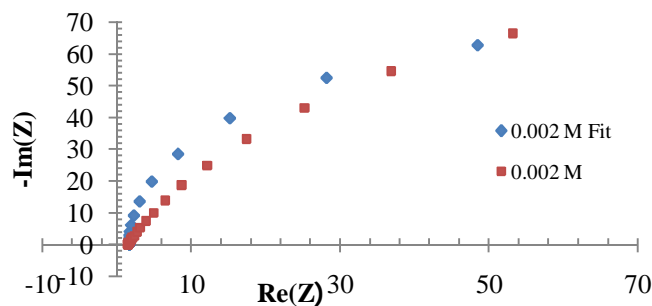


Figure 2: The Nyquist plots for corrosion of carbon steel in 1M HCl and his fit plot at 298 K

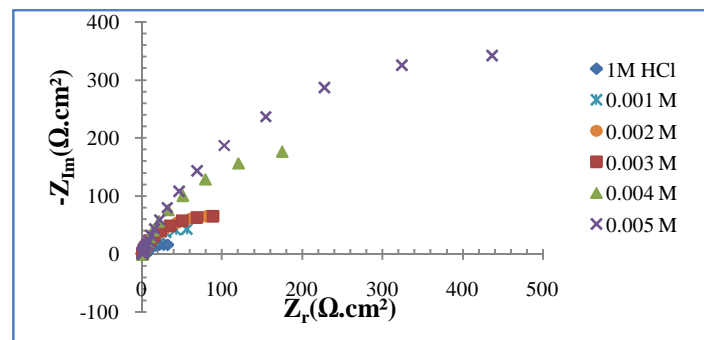


Figure 3: The Nyquist plots for corrosion of carbon steel in 1M HCl in the absence and presence of different Concentrations of DHQD at 298 K.

change in the corrosion mechanism occurs due to the inhibitor addition [29]. The high frequency loops are not perfect semicircles which can be attributed to the frequency dispersion as a result of the roughness and inhomogeneous of electrode surface [30]. The semicircles were obtained which cut the real axis at higher and lower frequencies. At higher frequency end, the intercept corresponds to solution resistance ( $R_s$ ) and at lower frequency end; the intercept corresponds to  $R_s + R_{ct}$ . The semicircle radii depend on the inhibitor concentration. The capacitive loop can be attributed to the charge transfer reaction and time constant of the electric double layer and to the surface inhomogeneity of structural or interfacial origin, such as those found in adsorption processes. Furthermore, the diameter of the capacitive loop in the presence of inhibitor is bigger than that in the absence of inhibitor (blank solution) and increases with the inhibitor concentration. This indicated that the impedance of inhibited substrate increased with increasing of the corrosion inhibitor concentration. The charge-transfer resistance ( $R_{ct}$ ) and the double layer capacitance ( $C_{dl}$ ) for the

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

inhibitor were determined by the analysis of the equivalent circuit models Figure 5, and their values for all samples at different DHQD concentrations are shown in

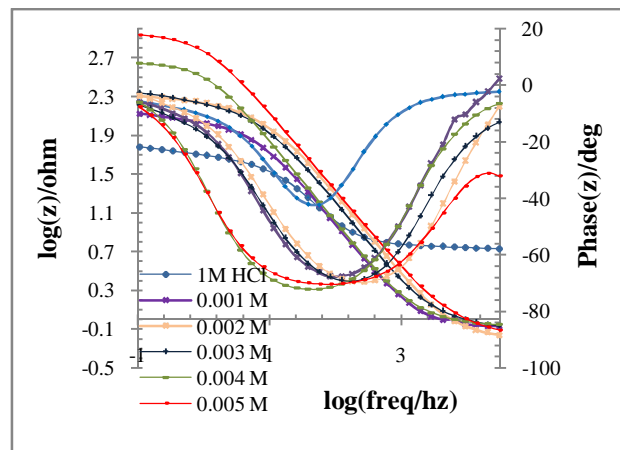


Figure 4: Bode plots of mild steel in different concentrations of DHQD in 1M HCl.

Table 3 inspection of the data in Table 3 reveals that DHQD appeared to act as an inhibitor over the studied concentration range,  $R_{ct}$  values increases, while those of  $C_{dl}$  decreases with increasing in DHQD concentration. This is due to increasing the surface. The  $R_{ct}$  values indicated that DHQD has a great effect on the dissolution of mild steel in HCl solution. This is due to increasing the surface coverage by the inhibitor which leads to an increase in the inhibition efficiency with increasing inhibitor concentration showing maximum inhibition 87,0 % as shown in Table 3. The decreasing in the capacitance, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, was suggested that the inhibitor molecules acted by adsorption at the

Table 3 Electrochemical parameters of impedance for carbon steel in 1 M HCl without and with of different concentrations of DHQD at 298 K.

C ( $10^{-3}M$ )	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$C_{dl}$ ( $F \text{ cm}^{-2} 10^{-6}$ )	A ( $S^n \Omega^{-1} \text{ cm}^{-2} 10^4$ )	n	$\omega\%$
Blank	55	1364	19,35	0,865	
1	78	557	8,04	0,883	29%
2	90	470	7,43	0,901	38%
3	181	348	4,82	0,882	69%
4	350	151	2,18	0,875	84%
5	649	114	1,52	0,889	91%

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

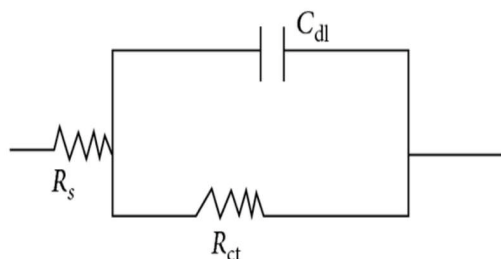


Figure 5. Suggested equivalent circuit model for the studied systems.

metal/solution interface In the Bode plots obtained without and with different concentrations of DHQD, it was found that the slopes of  $\log Z$  against  $\log f$  lines not equal  $-1$ , and the spectra consist one time constant. The high frequency part of the impedance and phase angle describes the behavior of an inhomogeneous surface layer, whereas the low-frequency component depicts the kinetic response to the charge transfer reaction [31].

### III.2. Gravimetric experiment

The loss in weight of mild steel in the presence and absence of HPCO at different concentrations and temperatures was determined, Table 1. From the Table, it was evident that there was a metal dissolution in the presence and absence of the inhibitor. It is pertinent to note however that the weight loss was higher in the absence of HPCO than its presence. The values of percentage inhibition efficiency  $\omega(\%)$ , corrosion rate  $V_{\text{corr}}$  ( $\text{g}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ), and the surface coverage ( $\theta$ ) obtained from weight loss measurements of mild steel after 6 h immersion are summarized in Tables 4 and 5. It was observed that HPCO inhibits the corrosion of mild steel in HCl solution, at all concentrations used in study i.e.  $1.5\cdot 10^{-3}$  M. weight loss of mild steel decreased with increasing inhibitor concentration. The results showed clearly that corrosion rate decreased significantly with addition of the inhibitor and then decreased gradually with increasing inhibitor concentration, while inhibition efficiency increased with increasing inhibitor concentration. Maximum inhibition efficiency was shown at  $5\cdot 10^{-3}$  M concentration of the inhibitor reached maximum value of 94 % at 298 K. It is evident from the Table 5 that the surface coverage is increased from 0,275 to 0,940. This behavior indicates that the adsorbed molecules formed a barrier film on the mild steel surface [32-36] and inhibit the corrosion processes via increasing the surface.

Table 4: Effect of DHQD concentration on corrosion data of mild steel in 1 M HCl

Conc. (M)	$\Delta M$			$V_{\text{corr}}$		
	298K	303K	308K	298K	303K	308K
Blank	0,082	0,166	0,250	0,0052	0,0104	0,0156
0,001	0,060	0,075	0,153	0,0037	0,0047	0,0096
0,002	0,054	0,0320	0,104	0,0034	0,0020	0,0065
0,003	0,026	0,028	0,088	0,0016	0,0018	0,0055
0,004	0,012	0,0180	0,065	0,0008	0,0011	0,0040
0,005	0,005	0,0160	0,049	0,0003	0,0010	0,0030

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

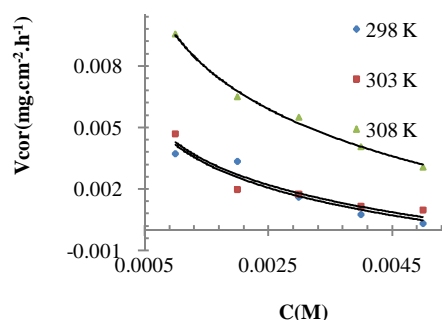
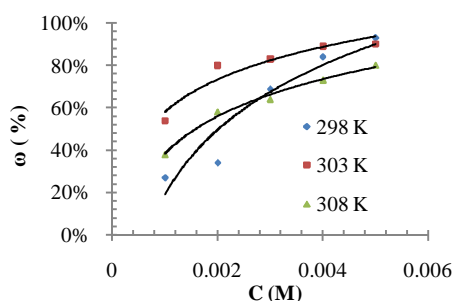
Vol. 6, Issue 1, January 2017

coverage of the electrode surface. The influence of solution temperature on inhibition efficiency showed that inhibition efficiency decreases with increase in temperature 298 K to 308 K. The decrease in inhibition efficiency with temperature may be attributed to desorption of the inhibitor. Corrosion rate of copper, aluminum and zinc have been the subject of many investigators [37-38]. Recent studies show that a strong coordination bond causes higher inhibition efficiency, the inhibition increasing in the sequence O < N < S < P [39]. Nitrogen and Sulphur.

Table 5: Corrosion parameters obtained of mild steel in 1M HCl solutions with and without addition of various concentrations of DHQD at different temperatures.

C (M)	Θ			ω (%)		
	298 K	303 K	308 K	298 K	303 K	308 K
Blank						
0,001	0,275	0,548	0,387	27,5%	54,8%	38,7%
0,002	0,347	0,809	0,582	34,7%	80,9%	58,2%
0,003	0,688	0,830	0,647	68,8%	83,0%	64,7%
0,004	0,850	0,893	0,739	85,0%	89,3%	73,9%
0,005	0,940	0,905	0,804	94,0%	90,5%	80,4%

containing compounds often provide excellent corrosion protection of mild steel in aggressive environment. For the inhibition of the carbon-steel corrosion in different media there have been used organic compounds containing sulphur, oxygen and nitrogen. The results show that most inhibitors act through adsorption on the metal surface. The investigation of DHQD gives excellent inhibitive performance in hydrochloric acid solutions. The good inhibitive performance in this study may be attributed to the presence of nitrogen as well as oxygen atom and double bonds in the same molecule. Organic inhibitors containing heteroatoms such O, N and S are found to have higher basicity and electron density and, thus, act as corrosion inhibitors. The heteroatoms are the active centers for the process of adsorption on the metal surface [40-42].



Figures 6-7: Dependence of the percentage inhibition efficiency ω (%) and corrosion rate on the inhibitor concentration

### III.3. Adsorption isotherms

Basic information on the interaction between the inhibitor molecules and the surface of mild steel can be provided by adsorption isotherm. Two main types of interaction can describe the adsorption of the organic compounds: physical adsorption and chemisorptions [43-45]. Adsorption isotherms are very important in determining the mechanism of



## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

organic electrochemical reactions. The mechanism of action of a corrosion inhibitor depends on the electron density and polarizability of the functional groups present in the molecule. To obtain more information about the mode of adsorption of DHQD onto the carbon steel surface, two adsorption isotherm models of Temkin and El Awady et al. thermodynamic kinetic were employed. The Temkin adsorption isotherm is given by [46-47]:

$$\exp(-2a\theta) = KC \quad (5)$$

Where  $K$  is the adsorption equilibrium constant and,  $a$  designates as the Frumkin lateral interaction parameter [48],  $\theta$  is the degree of surface coverage, and  $C$  is the concentration of the inhibitor. And the adsorption isotherm relationships of El Awady et al. thermodynamic kinetic were represented by the equation [49]:

$$\log \frac{\theta}{1-\theta} = \log K + y \log C \quad (6)$$

$$\Delta G_{ads}^0 = \Delta H_{ads}^0 - T\Delta S_{ads}^0 \quad (7)$$

where  $C$  is the concentration of the inhibitor,  $\theta$  is the degree of surface coverage,  $K$  is the equilibrium constant of adsorption process, and  $K = K^{1/y}$ .  $1/y$  is the number of inhibitor molecules occupying one active site (or the number of

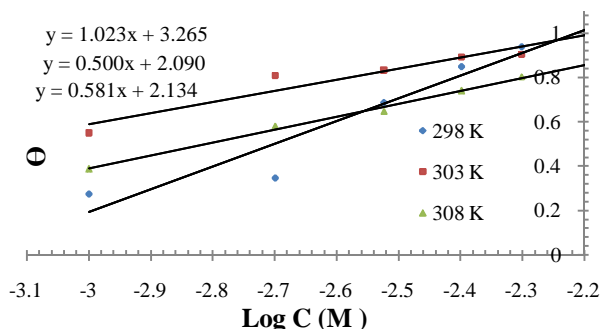


Figure 8: The plot of surface coverage ( $\theta$ ) as a function of logarithm of inhibitor concentration for mild steel in 1M HCl in the presence of DHQD at 298–308 K

water molecules replaced by one molecule of DHQD. Temkin adsorption parameters were recorded in Table 6. It indicated that the inhibitor obeys the Temkin model since the experimental data presents adequate

Table 6: Adsorption parameters for mild steel corrosion in the presence of DHQD in 1M HCl.

T (K)	a	1/a	R <sup>2</sup>	K	$\Delta G_{ads}^0$ (kJ.mol <sup>-1</sup> )	$\Delta H_{ads}^0$ (kJ.mol <sup>-1</sup> )	$\Delta S_{ads}^0$ (kJ.mol <sup>-1</sup> K <sup>-1</sup> )
298	0,9768	1,023	0,9059	24,284	-17,85	36,04	0,18
303	1,9976	0,501	0,9096	65,117	-20,69	36,04	0,18
308	1,7197	0,582	0,9927	39,270	-19,68	36,04	0,18

curve fitting for the applied adsorption isotherms. The calculated values of molecular interaction parameter,  $a$  and equilibrium constant of adsorption process,  $K$  obtained from Temkin plot are shown in Table 6. The positive ‘ $a$ ’ value indicated the steepness of the adsorption isotherm. The value of  $K$  value of the adsorption equilibrium constant relatively high reflects the high adsorption ability of this inhibitor on mild steel surface.

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

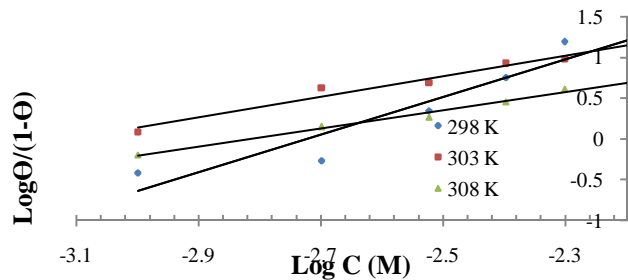


Figure 9: Curve fitting of the data of mild steel in 1M HCl in the Presence of DHQD to thermodynamic-kinetic El-Awady model Isotherm at different temperature.

Table 7: Adsorption parameters for mild steel corrosion in the presence of DHQD in 1M HCl.

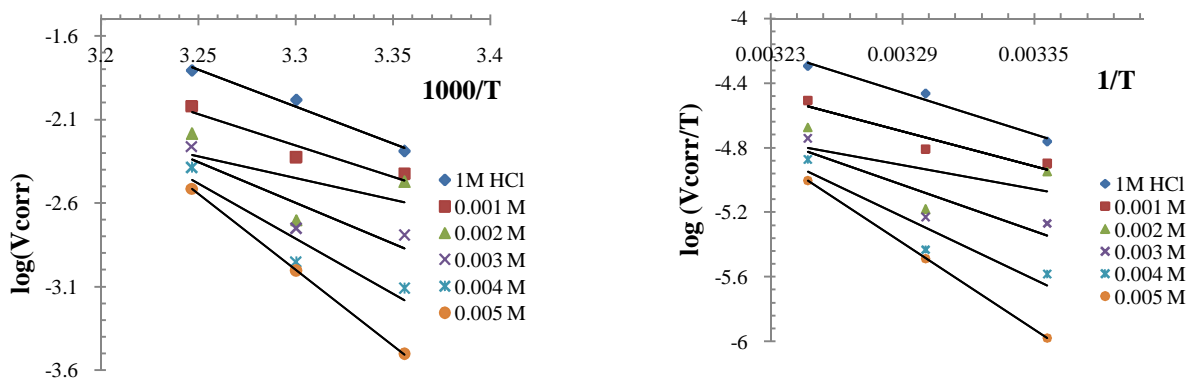
T(K)	1/y	y	R <sup>2</sup>	K
298	2,310	0,432	0,882	10 <sup>6</sup>
303	1,260	0,793	0,961	10 <sup>4</sup>
308	1,116	0,896	0,985	10 <sup>3</sup>

Curve fitting of the data to the thermodynamic-kinetic model is shown in Figure 9. This data gave straight lines with slopes equal to y. The values of 1/y and K calculated from the El-Awady model curve are given in Table 7. The values of 1/y obtained are more than unity indicating that DHQD involved in the adsorption process is attached to more than one active site on the metal surface. These values are approximately unity; implying one water molecule was replaced in the course of the inhibition process.

The equilibrium constant of the adsorption process K is related to the free energy of adsorption  $\Delta G_{ads}^0$  by:

$$K = \frac{1}{55.5} \times \exp\left(\frac{-\Delta G_{ads}^0}{RT}\right) \quad (8)$$

Where 55.5 is the molar concentration of water in solution. Adsorption equilibrium constants K and other thermodynamic parameters for the adsorption process that were obtained from these graphs are summarized in Table 7.



Figures 10-11: Arrhenius, Transition state plots for carbon steel dissolution in the absence and presence of DHQD

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

It is found that the  $\Delta G_{ads}^0$ , calculated by using the equation (8), values for the studied compound at higher temperature are less than  $-40 \text{ kJ mol}^{-1}$ , indicating that the DHQD is physically adsorbed on the metal surface [50]. Generally, the values of around  $-20 \text{ kJ mol}^{-1}$  or lower are consistent with physisorption, while those around  $-40 \text{ kJ/mol}$  or higher involve chemisorptions. The adsorption is enhanced by the presence the electron pairs in nitrogen as well as in oxygen and the delocalized  $\pi$  electrons in the inhibitor molecules they may interact with d-orbital of steel and adsorbed electrostatically forming stable film on the metal surface thus decreasing metal dissolution. It also revealed that the

Table 8: Activation energy and Arrhenius constant for mild steel in 1N HCl in absence and presence of DHQD.

C (M)	$\Delta H^0$ (kJ.mol <sup>-1</sup> )	$\Delta S^0$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )	$E_a$ (kJ.mol <sup>-1</sup> )	R <sup>2</sup>	Ea- $\Delta H^0$
Blank	82,17	-59,80	84,71	0,979	2,54
0,001M	69,13	-80,41	71,65	0,914	2,52
0,002M	47,35	-113,4	49,86	0,898	2,51
0,003M	90,96	-51,98	93,50	0,700	2,54
0,004M	124,24	-06,09	126,75	0,902	2,51
0,005M	171,66	-60,25	174,17	0,999	2,51

whole process was controlled by the surface reaction since the energy of the activation corrosion process in both the absence and presence of DHQD was greater than  $20 \text{ kJ mol}^{-1}$  [51]. As seen in Table 8, the values of  $\Delta H^0$  were the same, and the values of  $E_a$  increased for the corrosion of mild steel in the presence of DHQD suggesting that the energy barrier for the corrosion reaction increased in the presence of inhibitor without changing the dissolution mechanism. The high value of  $\Delta H^0$  ads in the case of DHQD in 1 M HCl indicated that this is more strongly adsorbed on the steel surface. The entropy of activation,  $\Delta S^0$ , the values of entropy of activation  $\Delta S^0$ , are large and negative. This implies that the activated complex in the rate determining step represent association rather than dissociation meaning that the decrease in a disordering takes place on going from reactants to activated complex [ 52-54 ].

#### III.4. Theoretical parameters predicating:

Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms [55]. Moreover, the gap between the LUMO and HOMO energy levels of the molecules was another important factor that should be considered. It has been reported that excellent corrosion inhibitors are usually those organic compounds who are not only offer electrons to unoccupied orbital of the metal, but



# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017



Figures 12-13-14: Optimized molecular structure, and HOMO and LUMO of investigated inhibitor.

also accept free electrons from the metal [56]. It is also well documented in literature that the higher the HOMO energy of the inhibitor, the greater its ability of offering electrons to unoccupied d-orbital of the metal, and the higher the corrosion inhibition efficiency. In addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the LUMO-HOMO energy gap decreased and the efficiency of inhibitor improved. The calculated

Table 9: Quantum-chemical descriptors for the studied compound

Compound	TE (u.a)	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$\Delta E_{\text{gap}}$ (eV)	$\mu$ (Debye)
DHQD	-568,45859	-6,664342	-4,301577	2,362765	6,2478

molecular properties for DHQD are presented in Table 9. Higher values of  $E_{\text{HOMO}}$  are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy or empty electron orbital. The negative coefficient of  $E_{\text{HOMO}}$  also confirms the physisorption mechanism [57].

The energy of the LUMO is directly related to the electron affinity and characterizes the susceptibility of the molecule towards attack by nucleophile. The lower the values of  $E_{\text{LUMO}}$  are, the stronger the electron accepting abilities of molecules. Low values of the energy gap ( $\Delta E$ ) will provide good inhibition efficiencies, because the excitation energy to remove an electron from the last occupied orbital will be low [58]. A molecule with a low energy gap is more polarizable and is generally associated with a high chemical reactivity.

Table 10: summarized the important global chemical parameters.

I : Ionisation energie (ev)	6,6643
A : Electronic affinity (ev)	4,3015
$\chi$ : Electronegativity (ev)	5,4829
$\eta$ : Hardness (ev)	1,1814
$\sigma$ : Softness ( $\text{ev}^{-1}$ )	0,8464

Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules [59]. The low ionization energy 6.6643 (eV) of DHQD indicates the high inhibition efficiency.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

large energy gap and a soft molecule has a small energy gap [60]. Soft molecules can easily change both their number of electrons and the distribution of charge within the molecule. Taking our molecule as the prototype, the value of  $\chi = 5.4829$  eV shows that it is primarily an electron donor, or a base. A value  $\eta = 1.1814$  eV is relatively low, which shows that the molecule is relatively soft, so that our molecule can easily change both the number of Electron and load distribution in the molecule. [61]

## IV. CONCLUSIONS

1. 1,4-dihydroquinoxaline-2,3-dione can effectively inhibits mild steel corrosion in Hydrochloric Acid, the inhibition efficiency increases with inhibitor concentration at all temperatures studied and decreases with rise in temperature
2. The Tafel plot indicates that DHQD act as a mixte inhibitor
3. The adsorptive behavior may be approximated by Temkin and Al-Awady adsorption isotherms.
4. The energy of activation increased in the presence of DHQD suggesting that the energy barrier for the corrosion reaction increased in the presence of inhibitor without changing the dissolution mechanism
5. A low energy gap indicates that DHQD is more polarizable and is generally associated with a high chemical reactivity.

## REFERENCES

- [1] L. Larabi, Y. Harek, M. Traisnel, A. Mansri, "Inhibition behavior of mild steel in 1 M HCl in the presence of poly(4-vinylpyridine) (P4VP) and potassium iodide", *J. Appl. Electrochem.* 34, pp. 833-839, 2004.
- [2] H. M. Bhajiwala and R. T. Vashi, "Ethanolamine, Di-ethanolamine and triethanolmine as Corrosion Inhibitors for Zinc in Binary Acid Mixture ( $\text{HNO}_3 + \text{H}_3\text{PO}_4$ )", *Bul-letin of Electrochemistry*, Vol. 17, pp. 441-448, 2001.
- [3] G.N. Mu, X. Li, F. Li, Synergistic inhibition between o-phenanthroline and chloride ion on cold rolled steel corrosion in phosphoric acid, *Mater. Chem. Phys.* 86, pp. 59-68, 2004.
- [4] E.E. Ebenso, Synergistic effect of halide ions on the corrosion inhibition of aluminium in  $\text{H}_2\text{SO}_4$  using 2-acetylphenothiazine, *Mater. Chem. Phys.* 79, pp 58-70, 2003.
- [5] G.K. Gomma, Corrosion of low carbon steel in sulphuric acid solution in presence of pyrazole-halide mixture, *Mater. Chem. Phys.* 55, pp 241-246, 1998.
- [6] H. Ashassi-Sorkhabi, S.A. Nabavi-Amri, Corrosion inhibition of carbon steel in petroleum/water mixtures by n-containing compounds, *Acta Chim. Slov.* 47, pp 507-517, 2000.
- [7] M. Abdallah, M. Al-Agez, and A. S. Fouda, "Phenylhydrazone derivatives as corrosion inhibitors for  $\alpha$ -brass in hydrochloric acid solutions," *International Journal of Electrochemical Science*, vol. 4, no. 3, pp. 336-352, 2009.
- [8] M. Bouklah, N. Benchat, A. Aouniti et al., "Effect of the substitution of an oxygen atom by sulphur in a pyridazinic molecule towards inhibition of corrosion of steel in 0.5M $\text{H}_2\text{SO}_4$  medium," *Progress in Organic Coatings*, vol. 51, no. 2, pp. 118-124, 2004.
- [9] H.L. Wang, R.B. Liu, and J. Xin, "Inhibiting effects of some mercapto-triazole derivatives on the corrosion of mild steel in 1.0M HCl medium," *Corrosion Science*, vol. 46, no. 10, pp. 2455-2466, 2004.
- [10] M. Karakus, M. Sahin, and S. Bilgic, "An investigation on the inhibition effects of some new dithiophosphonic acid monoesters on the corrosion of the steel in 1M HCl medium," *Materials Chemistry and Physics*, vol. 92, no. 2-3, pp. 565-571, 2005.
- [11] A.A. Rahim, E. Rocca, J. Steinmetz, M. J. Kassim, R. Adnan, and M. S. Ibrahim, "Mangrove tannins and their flavanoid monomers as alternative steel corrosion inhibitors in acidic medium," *Corrosion Science*, vol. 49, no. 2, pp. 402-417, 2007.
- [12] W. Li, Q. He, C. Pei, and B. Hou, "Experimental and theoretical investigation of the adsorption behaviour of new triazole derivatives as inhibitors for mild steel corrosion in acid media," *Electrochimica Acta*, vol. 52, no. 22, pp. 6386-6394, 2007.
- [13] H. El attari, K. Lahmadi and M. Siniti. Adsorption and Inhibitive Properties of Tetradecyltrimethylammonium Chloride for the Corrosion of Carbon Steel in Acid Sulfuric, *International Journal of Latest Trends in Engineering and Technology (IJLTET)*. Vol. 6 n<sup>o</sup>2, pp. 423-434, 2015.
- [14] H. El Attari, A. El Bribri, L. Mhaidra, F. Bentiss and M. Siniti. Synthesis and Anticorrosion for Carbon Steel of 4-Amino-3, 5 Bis (4-Hydroxy-3-Methoxy)-1, 2, 4-Triazole in Hydrochloric Acid Solution. *American Journal of Engineering Research*, Volume-4, Issue-3, pp. 44-51, 2015.
- [15] B. Mernari, H. El attari, M. Traisnel, F. Bentiss, M. Lagrenee, Inhibiting effects of 3, 5-bis (n-pyridyl)-4-amino-1, 2, 4-triazoles on the corrosion for mild steel in 1 M HCl medium. *Corros. Sci.* 40, pp.391-399, 1998.
- [16] S. Foudaa, A. El-Bendaryb, M. Diabb, A. Bakr, Inhibition of corrosion of carbon steel in 0.5 m HCl solutions by some pyridopyrimidine derivatives, *Mor. J. Chem.* 2 N<sup>o</sup>4, pp.302-319, 2014.
- [17] H. El attari, K. Lahmadi, A. El bribri and M. Siniti, The Adsorption and Corrosion Inhibition of Non-Ionic Surfactant on Carbon Steel Surface in Hydrochloric Acid, *International Journal of Materials and Chemistry* : 5(3), pp.77-83,2015.
- [18] A. El bribri, M. Tabyaoui, H. El Attari, K. Boumhara, M. Siniti, B. Tabyaoui, " Temperature effects on the corrosion inhibition of carbon steel in HCl (1M) solution by methanolic extract of Euphorbia Falcata.L", *J. Mater. Environ. Sci.* 2 (2), pp. 156-165, 2011.

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

- [19] H. El attari, K. Lahmadi, S.Mengouch, A. Khribech, L.Khamliche , M. Siniti, Kinetics and Thermodynamic Study of Inhibition, Potentials by 3-Acetyl-4-Oxo-Benzopyranone on Mild Steel in H<sub>2</sub>SO<sub>4</sub> Solution and Synergistic Effect of Chloride Ions, International Journal of Innovative Research in Science, Engineering and Technology, Vol. 5, Issue 2, February, pp. 1848-1861, 2016.
- [20] A. Anejjar, R. Salghi, S. Jodeh, S. S. Al-Deyab, B. Hammouti. A. M. Elhassan , Inhibitive Action of Hydroxylammonium Sulfate on the Corrosion of Carbon Steel in Hydrochloric Acid Medium and their Adsorption Characteristics, Mor. J. Chem. 2 n°3 pp., 236-25, 2014.
- [21] M. Palomar, M. Romo, H. Hernández , M. Abreu-Quijano, N. Likhanova , et al. Influence of the alkyl chain length of 2 amino alkyl 1, 3, 4, thiazazole compounds on the corrosion inhibition of Steel immersed in sulfuric acid solutions. Corros Sci 54, pp 231-243, 2012.
- [22] A. Popova, M. Christov, A. Zvetanova, Effect of the molecular structure on the inhibitor properties of azoles on mild steel corrosion in 1M hydrochloric acid. Corros Sci 49, pp 2131-2143, 2007.
- [23] M. Elayyachy, M. Elkodadi, A. Aouniti, A. Ramdani, B. Hammouti, et al. New bipyrazole derivatives as corrosion inhibitors for steel in hydrochloric acid solutions. Mat Chem Phys 93, pp 281-285, 2015.
- [24] I. Danaee, M. Gholami, M. RashvandAvei, H. Maddahy Quantum chemical and experimental investigations on inhibitory behavior of amino-imino tautomeric equilibrium of 2-aminobenzothiazole on steel corrosion in H<sub>2</sub>SO<sub>4</sub> solution. J Ind Eng Chem 26, pp 81-94, 2015.
- [25] M. Bouklah, A. Attayibat, S. Kertit, A. Ramdani, B. Hammouti, A pyrazine derivative as corrosion inhibitor for steel in sulphuric acid solution. App Surf Sci 242, pp 399-406, 2005.
- [26] M. Awad, Eco-friendly corrosion inhibitors, Inhibitive action of quinine for corrosion of low carbon steel in 1M HCl. J of Appl Electrochem 36, pp 1163-1168, 2006.
- [27] J. Thompson, E. Scheetz, R. Schock, A. Lytl, J. Delaney, Abstracts, Water Quality Technology Conference, Denver, 1997.
- [28] S. Hari Kumar, S. Karthikeyan, Inhibition of mild steel corrosion in hydrochloric acid solution by cloxacillin drug. J. Mater. Environ. Sci. 3, (5), pp 925-934, 2012.
- [29] J. Hmimou , A. Rochdi , R. Tourir , M. Ebn Touhami , E. H. Rifi , A. El Hallaoui , A. Anouar , D. Cheba, Study of corrosion inhibition of mild steel in acidic medium by 2-propargyl-5-p-chlorophenyltetrazole, J. Mater. Environ. Sci. 3, (3), pp 543-550, 2012.
- [30] R Prabhu, A Shanbhag, T Venkatesha, Inhibition Effects of a Synthesized Novel 4-Aminoantipyrine Derivative on the Corrosion of Mild Steel in Hydrochloric Acid Solution together with Quantum Chemical Studies, J. Appl. Electrochem. 37, pp 491-497, 2007.
- [31] Y. Chen, T. Hong, M. Gopal, W.P. EIS studies of a corrosion inhibitor behavior under multiphase flow conditions, Japson Corrosion Science 42, pp 979-990, 2000.
- [32] J. Hmimou, A. Rochdi, R. Tourir, M. Ebn Touhami, E. H. Rifi, A. El Hallaoui, A. Anouar, D. Chebab, Study of corrosion inhibition of mild steel in acidic medium by 2-propargyl-5-p-chlorophenyltetrazole: Part I, J. Mater. Environ. Sci. 121, pp 543-550, 2009.
- [33] A. Salman Al-zubidy, A. Hummza, Corrosion Behavior of Copper and Carbon Steel in Acidic Media, Baghdad Science Journal. Vol.11(4), pp 1577- 1582, 2014.
- [34] X. Pang, M. Gong, Y. Zhang, Q. Wei, Corrosion inhibition and mechanism of mild steel in hydrochloric acid by ceftriaxone and amoxicillin Corros. Science China Chemistry, Volume 54, Issue 9, pp 1529-1536, 2011.
- [35] C.A. Schiller, W. Strunz, The evaluation of experimental dielectric data of barrier coatings by means of different models Electrochim. Acta, 46, pp 3619-3625, 2001.
- [36] D.A. Lopez, S.N. Simison, S.R. de Sanchez, The influence of steel microstructure on CO<sub>2</sub> corrosion. EIS studies on the inhibition efficiency of benzimidazole, Electrochim. Acta, 48, pp 845-854, 2003.
- [37] H. M. Bhajiwala and R. T. Vashi, "Ethanalamine, Di-ethanolamine And triethanolmine as Corrosion Inhibitors for Zinc in Binary Acid Mixture (HNO<sub>3</sub> + H<sub>3</sub>PO<sub>4</sub>)," Bul-letin of Electrochemistry, Vol. 17, pp. 441- 448, 2001.
- [38] E. Cano, J. Polo, A. La Iglesia, J. Bastidas, A study on the adsorption of benzotriazole on copper in hydrochloric acid using the inflection point of the isotherm, Adsorption 10, pp. 219-225, 2004.
- [39] G. Trabaneli, Etude de l'effet des alcaloïdes sur la corrosion de l'acier C38 en milieu acide chlorhydrique 1M Corrosion Mechanisms, F. Mansfeld editor, Marcel Dekker, New York, pp 119-131, 1987.
- [40] A. Ghazoui, N. Bencat, S. Al-Deyab, A. Zarrouk, B. Hammouti, M. Ramdani, M. Guenbour, An Investigation of Two Novel Pyridazine Derivatives as Corrosion Inhibitor for C38 Steel in 1.0 M HCl, Int. J. Electrochem. Sci. 8, pp 2272 – 2292, 2013.
- [41] M.A. Quraishi, D. Jamal, Inhibition of mild steel corrosion in the presence of fatty acid triazoles 3rd European Symposium on Corrosion Inhibitors, Journal of Applied Electrochemistry, Volume 32, Issue 4, pp 425-430, 2002.
- [42] Q.B. Zhang, Y.X. Hua, Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid, Electrochim. Acta, 54, pp 1881-1887, 2009.
- [43] L. Larabi, Y. Harek, M. Traisnel, A. Mansri, "Inhibition behavior of mild steel in 1 M HCl in the presence of poly(4-vinylpyridine) (P4VP) and potassium iodide" , J. Appl. Electrochem. 34, pp. 833-839, 2004
- [44] S.A. Umoren, O. Kinetics and Thermodynamic Study of Inhibition Potentials by 3-Acetyl-4-Oxo-Benzopyranone on Mild Steel in H<sub>2</sub>SO<sub>4</sub> Solution and Synergistic Effect of Chloride Ions Electrochem. 22, pp. 155-157, 2006.
- [45] G.N. Mu, X.M. Li, G.H. Liu, G.N. Mu, X.M. Li, G.H. Liu, Corros. Sci. 47, pp. 1932-1952, 2005. Corros. Sci. 47, pp. 1932-1952, 2005.
- [46] Damaskin, B.B., Petrii, O.A., Batrakov, B., Adsorption of organic compounds on electrodes, Plenum Press, New York, 1971.
- [47] Langmuir, I, the constitution and fundamental properties of solids and liquids J. Amer. Chem. Soc. 39, pp1848-1906, 1947.
- [48] Frumkin, A.N, Comparison of the van der Waals and Frumkin Adsorption Isotherms for Sodium Dodecyl Sulfate at Various Salt Concentrations Z. Phys. Chem., 16, pp 466, 1925.
- [49] Hill de Boer, the Dynamical character of adsorption, 2nd Edition, Clarendon Press, Oxford, UK, 1968.
- [50] W.W. Damaskin, O.A. Pietrij, W.W. Batrakov, "Adsorption of organic compounds on electrode", Plenum Press", New York, 1997.
- [51] I. Putilova, S. Balezin, V. Barannik, Corrosion Inhibition of C38 Steel in 1 M HCl: A Comparative Study of Black Pepper Extract and Its Isolated, Metall. Corros. Inhibi. Pergamon Press, New York, pp 31, 1960.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

- [52] Z. Hadi, M Al-Sawaad, Thermodynamic and quantum chemistry study for dimethylol-5-methyl Hydantoin and its derivatives as corrosion inhibitors for carbon steel N-80 in raw water, *J. Mater. Environ. Sci.* 2 (2), pp 128-147, 2011.
- [53] J. Bockris, B. Yang, The mechanism of corrosion inhibition of iron in acid solution by acetylenic alcohols, *J. Electrochem. Soc.* 138, pp 2237–2252, 1991.
- [54] M.S .Al-Otaibi., A. Al-Mayouf, Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media, *Arabian Journal of Chemistry*, 7, (3), pp 340–346, , 2014,
- [55] C. Selles, O. Benali, B. Tabti, L. Larabi, Y., Harek Green corrosion inhibitor: inhibitive action of aqueous extract of *Anacyclus pyrethrum* L. for the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, *J. Mater. Environ. Sci.*, 3, pp 206-219, 2012,
- [56] S. Hosseini, S. Eftekhari, M. AMIRI, Polarization Behaviour of Stainless Steel Type 302 in HCl Solution of Benzotriazole, *Asian Journal of Chemistry*, 19, No. 4, pp 2574-2580, 2007.
- [57] Popova A., “Temperature effect on mild steel corrosion in acid media in presence of azoles,” *Corrosion Science*, vol. 49, , pp 2144–2158, 2007.
- [58] P. Chao, Q Liang, Y Li, Electrochemical and Quantum Chemical Studies of 1, 5-bis (2-nitrophenyl)-1, 4-pentadien-3-one as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution, *Appl. Surf. Sci.*, 252 pp 1596, 2005.
- [59] I.B Obot., N.O .Obi-Egbedi, Corrosion inhibition and adsorption behaviour for aluminum by extract of *Aningeria robusta* in HCl solution: Synergistic effect of iodide ions, *J. Mater. Environ. Sci.* 2 (1), pp 60-71, 2011,
- [60] A. Zarrouk, H. Zarrouk, L. Salghi, F. Bentiss, Evaluation of N-containing organic compound as corrosion inhibitor for carbon steel in phosphoric acid, *J. Mater. Environ. Sci.* 4 (2), pp 177-192, 2013.
- [61] R. Kumar, R. Karthik, S. Chen, Electrochemical and Quantum Chemical Studies of 1, 5-bis (2-nitrophenyl)-1, 4-pentadien-3-one as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution, *Int. J. Electrochem. Sci.*, 11, 8892 – 8913, 2016.