International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

# **Corrosion Inhibition Performance and Adsorption Mechanism of Novel Quinazoline Schiff Base on Low Alloy Steel in HCl Media**

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Received: 27 July 2018 / Accepted: 21 September 2018 / Published: 5 November 2018

The inhibition performance of synthesized Quinazoline Schiff Bases 2-(3,3-Dimethyl-2,3-dihydroindol-2-ylidene)-3-[(2-hydroxyphenyl) imino] propylidene (DHIP1) and 2-(3,3-Dimethyl-2,3-dihydroindol-2-ylidene)-3-[(2-hydroxyphenly) imino] propanal (DHIP2) on low carbon steel (LAS) in 1 M HCl has been examined using weight loss, electrochemical measurements and scanning electron microscopy (SEM). The obtained experimental results indicated that both DHIP1 and DHIP2 have fairly enhanced the corrosion resistance of LAS and extremely exhibited better inhibitive efficiencies at a concentration of 5 mM. The results of potentiodynamic polarization results clarified that investigated Schiff Bases acts as mixed-type inhibitors and follow Langmuir adsorption isotherm is fitted well for adsorption. It was found that the inhibition efficiency increases with increase in inhibitor concentration as confirmed by all the measurements.

Keywords: Low alloy steel; inhibition corrosion; adsorption; EIS; Quinazoline Schiff Bases

# **1. INTRODUCTION**

Low Alloy Steel is one of the most commonly used engineering materials for storage and construction, ease of fabrication, low cost affordability and abundance. Moreover, it also provides

excellent physical properties that are suitable for a variety of industrial and mechanical application [1, 2]. As a result of corrosion, the deterioration and even in extreme conditions, the failure of LAS equipment occur, during oil well acidification, gas production systems, oil storage and transportation of oil etc. through pipelines. Consequences of corrosion leads to huge economic damage nation's GDP [1, 3]. The addition of corrosion inhibitor is one promising strategy for mitigating corrosion of LAS in acidic medium. A variety of corrosion inhibitors are enormously used in very small concentration in order to lower the corrosion rate of steel [4 - 7]. Although several synthetic and toxic compounds like chromate, polyphosphates, benzothaizole have been proved as effective corrosion inhibitors, but due to their toxic, non-biodegradable nature and expensive too, moreover, their applications have been limited as corrosion inhibitors [8]. Due to the existence of heteroatoms like nitrogen, oxygen and sulfur as well as aromatic ring structure or containing pi electrons in their molecular structure with high electron density in most of the organic compounds enable them to reveal as excellent corrosion inhibitors [9, 10]. Review of literature have been reported the application of Schiff base compounds as excellent corrosion inhibitors for the inhibition of copper, steel and aluminum in acidic medium solutions [11 - 13]. Generally, the effectiveness of Schiff bases is based due to the tendency of strong adsorption at metal interface, causing to block the active corrosion sites, leading the metal shielding from the acidic solution and finally impedes the metal decomposition. Usually, the inhibitions of these organic compounds as corrosion inhibitor are attributed to the mutual interaction of the substrate surface through adsorption process. [14]. In addition, adsorption process depends on the adsorption mode, the sort of inhibitor chemical structure, electrolyte solution and the metal surface charge [15].

In this study the inhibition of LAS corrosion in 1 M HCl solution by two Quinazoline Schiff Bases (abbreviated as DHIP1 and DHIP2) has been studied using gravimetric and electrochemical measurements. The investigated compounds have shown high inhibition efficiency against LAS corrosion in 1 M HCl solution due to strong adsorption onto the metal surface due to its heterocyclic nature constituting a diversity of donor atoms. The inhibition efficiencies on the basis of compounds structure and the SEM analysis were also included in the present research work.

#### 2. EXPERIMENTAL

#### 2.1 Material

Table 1.	Chemical	composition	of low	alloy steel	(wt. %)
		1		2	· /

С	Si	S	Р	Mn	Ni	Cr	Cu	Mo	V	W	Fe
0.337	0.163	0.046	0.053	0.813	0.102	0.178	0.036	0.018	0.0046	0.0021	Bal.

LAS with a thickness of 0.25 cm were used as experimental metal. The chemical composition of the investigated material is listed in Table 1. The electrodes were then subsequently ground with 800, 1200 and 1500 grit silicon carbide paper follow by thoroughly washing with distilled water, degreased in acetone and dried by hot flowing air.

Rectangular shape LAS specimens having dimensions of 2.0 cm x 2.0 cm x 0.05 cm were immersed in the aggressive solution for a time period of 6 h at  $25 \pm 1$  °C in order to calculate the weight loss measurements. Later the immersion period the test specimens were cleaned following ASTM G-81, reweighted using analytical balance ( $\pm$  0.1 mg) to determine the corrosion rate [16, 17]. The test solutions were prepared by dilution (37% HCl, Merck, density 1.185) analytical grade. The molecular formulas of the investigated Schiff Bases are shown in Fig.1.



**Figure 1.** The chemical structure of 2-(3,3-Dimethyl-2,3-dihydro-indol-2-ylidene)-3-[(2-hydroxyphenyl) imino] propylidene (DHIP1) and 2-(3,3-Dimethyl-2,3-dihydro-indol-2-ylidene)-3-[(2-hydroxyphenly) imino] propanal (DHIP2)

#### 2.2 Weight loss measurements

The average weight loss in the terms of mean corrosion was calculated and expressed in mg cm<sup>-2</sup> h<sup>-1</sup>. The inhibition efficiency ( $\eta_{WL}$ %) is calculated using the following relation (1) [18]:

$$\eta_{WL}\% = \frac{W_{corr}^0 - W_{corr}}{W_{corr}^0} X \ 100 \tag{1}$$

Where  $W_{corr}^0$  and  $W_{corr}$  are corrosion rate without and with the presence of inhibitors, respectively. The weight loss measurements was used to work out the corrosion rate (mm per year) and surface coverage ( $\theta$ ) utilizing equations (2) and (3) [19] respectively.

$$CR = \frac{87.6 X \Delta W}{\rho.A.T} \tag{2}$$

$$\theta = \frac{W - W_{inh}}{W} \tag{3}$$

Where  $\Delta W$  is the average weight loss (mg),  $\rho$  and A denote the density (gcm<sup>-3</sup>) and exposed surface area (cm<sup>2</sup>) of specimen and T represent the exposure time (h) of immersed specimens.

Similarly, W (mg) and  $W_{inh}$  (mg) are the weight losses data obtained from the acidic solution without and with the presence of inhibitor respectively.

#### 2.3 Electrochemical measurements

Electrochemical measurements were achieved utilizing a conventional three electrode cell with a working electrode (LAS), a platinum wire as a counter electrode as well as saturated calomel electrode (SCE) as reference electrode respectively. The software like General purpose electrochemical software (GPES) and Frequency response analysis (FRA) were used for measuring anodic and cathodic Tafel curves and EIS measurements along with open circuit potential (OCP) methods. These electrochemical methods were performed using an (AUTOLAB PGSTAT 30, Netherlands) instrument. The current-potential range for potentiodynamic polarization method were between +0.3 to -0.3 V SCE at a scan rate of 0.1 mV/s. The impedance measurements were controlled by the FRA- 3.5 software in a frequency range of 100 kHz – 10 mHz with an AC wave of  $\pm 5$  mV peak to peak. The impedance information data were acquired at a rate of 10 points per decade change in frequency. Prior to all electrochemical estimations the working electrodes were immersed into the test solution containing inhibitors at various concentration for a time period of 60 minutes in order to build up a steady state open circuit potential (E<sub>ocp</sub>).

The anodic and cathodic Tafel curves were extrapolated in order to attain the corrosion potential  $(E_{corr})$  and corrosion current density  $(I_{corr})$ . The inhibition efficiencies from potentiodynamic polarization (PDP) IE<sub>P</sub> (%) and electrochemical impedance spectroscopy (EIS) IE<sub>EIS</sub> (%) were computed using equations (4) and (5) respectively [20, 21]:

$$IE_P(\%) = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} X \ 100$$
 (4)

Where  $I_{corr}^{o}$  and  $I_{corr}$  are the corrosion current densities for LAS electrodes in the uninhibited and inhibited solutions respectively.

$$IE_{EIS}(\%) = \left(1 - \frac{R_{CT}^0}{R_{CT}}\right) X \ 100$$
 (5)

Where  $R^{o}_{ct}$  and  $R_{ct}$  are the charge transfer resistance in the absence and the presence of inhibitors respectively.

#### 2.4 Scanning Electron Microscope (SEM) studies

The surface morphology of LAS was studied using a JEOL JSM-840A scanning electron microscope at an accelerating voltage of 10 KeV. Images of the specimens were recorded after 6 h immersion time in 1 M HCl solution in the absence and presence of 5 mM of investigated Schiff Bases (DHIP1 and DHIP2) inhibitors at  $25 \pm 1$  °C.

## **3. RESULTS AND DISCUSSION**

#### 3.1 Weight loss and inhibition efficiency measurements

The weight loss measurements were conducted in a glass cell to measure the metal dissolution rate as a function of time in 1M HCl solution for LAS coupons without and with the different concentrations of the Schiff Bases (0.5 mM, 1.5 mM, 3 mM and 5 mM). The initial and the final weight of the specimen were recorded using a digital balance (precision  $\pm$  0.1 mg). It is seen from the Fig.2 that the weight loss of LAS specimen increases in HCl solution in the absence of inhibitors with the passage of time as a result of continuous dissolution of metal ions [22, 23]. However, the addition of 0.5 mM of Schiff Bases significantly lower the weight loss of LAS and its effects extremely increases with increasing the concentration of Schiff Bases as obvious in Fig. 2.



**Figure 2.** Variation of weight loss with time for the corrosion of low alloy steel (LAS) in 1 M HCl containing various concentrations of HDIPs at 298 K.

This phenomenon is attributed to the adsorption of Schiff Bases (DHIP1 and HDIP2) molecules on the active metal sites preventing the direct corrosion ions attack leading the metal protection from the corrosive solution [24, 25]. Data for corrosion rate (CR), surface coverage ( $\theta$ ) and inhibition efficiency IE<sub>WL</sub> (%) were summarized in Table 2. It is clearly seen that increasing the Schiff Bases concentration distinctly raises and lowering the values of CR. The maximum inhibition efficiency was achieved by 5 mM HDIP1 after 6 hours and recorded as 85%. Further increasing the concentration from 0.5 mM to 5 mM (HDIP1 and HDIP2) an increase of 82% and 85% were observed leading a decrease in weight loss (corrosion rate) and increasing the degree of surface coverage and collectively inhibit the inhibition efficiencies. The maximum inhibition efficiency for each inhibitor at a concentration of 5 mM was observed. Further increase in concentration exhibited a marginal change in the inhibitors performance. Therefore, the optimum inhibitor concentrations of the investigated inhibitors were established to be 5 mM.

Inhibitor concentration (mM)	Corrosion rate $(mg cm^{-2} h^{-1})$	θ	IE <sub>WL</sub> (%)
Blank (B)	8.07	-	-
B + 0.5 mM HDIP1	6.74	0.4715	47.15
B + 1.5 mM HDIP1	5.82	0.6428	64.28
B+ 3 mM HDIP1	4.12	0.7322	73.22
B + 5  mM HDIP1	2.65	0.8553	85.53
Blank (B)	8.07		
B + 0.5 mM HDIP2	6.98	0.4433	44.33
B + 1.5 mM HDIP2	6.02	0.6188	61.88
B + 3  mM HDIP2	3.57	0.7153	71.53

2.91

0.8012

80.12

**Table 2.** Corrosion rate and inhibition efficiencies of LAS steel in 1 M HCl solution at concentrations of HDIPi and HDIP2 at 298K.

3.2 Open circuit potential (OCP) measurements

B + 5 mM HDIP2



**Figure 3.** Open circuit potential (OCP) as a function of different concentration of HDIP1 and HDIP2 for 60 min for LAS in 1 M HCl.

The deviation of OCP of LAS in 1 M HCl solution with and without inhibitors over time is shown in Fig. 3. According to Fig. 3 it can be witnessed that after a scanning time period of 60 minutes, the presence of inhibitors result in a more positive shift in the OCP values at all the concentrations. The consequences of the OCP shift suggest that both Quinazoline Schiff Bases have the capacity to hinder the corrosion of LAS in HCl medium. Moreover, the positive shift in OCP values with increasing inhibitor concentration recommend the strength of the adsorbed apparent layer of the investigated inhibitors [26]. After an immersion of 45 minutes, the investigated systems accomplish a steady state condition.

#### 3.3 Galvanostatic potentiodynamic polarization

Electrochemical polarization techniques are commonly used for understanding the mechanism and classifying the possible working principle of the investigated additives on the structure of half reaction (anodic and cathodic) [27].



**Figure 4.** Corrosion polarization plots for LAS in 1 M HCl without and with Quinazoline Schiff bases (HDIP1 and HDIP2) at 298 K.

The polarization curves of the LAS electrodes in 1 M HCl solution comprising (1) Blank (2) 0.5 mM, (3) 1.5 mM (4) 3 mM and (5) 5 mM of Quinazoline Schiff Bases (HDIP1 and HDIP2) after a time 6 h of electrodes immersion are shown in Fig. 4.

From Fig. 4 it was revealed that both anodic and cathodic curves were shifted to the region of lower values as compared to the blank solution after adding the inhibitors (HDIP1 and HDIP2) to the corrosive medium. Furthermore, the addition of the inhibitors does not change the nature of the polarization curves in both inhibited and uninhibited solutions indicating that the mechanism of the

corrosion process remains almost same. The electrochemical parameters including: corrosion potential  $(E_{corr})$ , corrosion current density  $(i_{corr})$ , anodic and cathodic Tafel slopes (ba and bc) and potentio dynamic corrosion inhibition efficiency  $(IE_{PD})$  as a function of investigated inhibitors concentration at  $25 \pm 1^{\circ}$ C are summarized in table 3.

The potentiodynamic parameters listed in Table 3 indicate that increasing the inhibitor concentration a net decrease in the  $i_{coor}$  values and the shifting the  $E_{corr}$  values in more positive direction were obtained since the capability of the inhibitors molecules are improved to in order to isolate the active sites responsible for the corrosion reaction [28, 29]. It can be inferred that the both the investigated Schiff Bases (HDIP1 and HDIP2) may act as mixed type inhibitors in HCl medium retarding both anodic dissolution of LAS specimen and cathodic evolution of hydrogen gas [30].

Inhibitors	Concentration	Ecor	ba	bc	i <sub>corr</sub>	IEpd
	(mM)	(mV vs. SCE)	(mV/dec)	(mV/dec)	(µAcm-2)	(%)
Blank	-	523	-	-	372.3	-
HDIP1	0.5	470	95.2	112	168.6	50.1
	1.5	452	86.7	126.5	86.9	63.2
	3	438	82.2	113.2	62.7	76.5
	5	432	82.6	101.2	62.1	86.3
HDIP2	0.5	491	85.6	102.7	165.1	47.9
	1.5	479	71.7	91.5	85.7	61.3
	3	455	74.3	93.4	61.2	75.1
	5	450	73.8	93.1	60.3	81.8

**Table 3.** Polarization parameters of LAS in 1 M HCl solution of various concentrations of Quinazoline

 Schiff Bases at ambient temperature

## 3.4 EIS measurements

EIS measurements were employed to confirm the data attained by polarization techniques. In addition, EIS was effectively carried out to describe the corrosion behavior and corrosion inhibition mechanism in chloride medium [31, 32]. Fig. 5 represents the Nyquist plot of EIS spectra of the LAS electrodes in 1 M HCl solution in the absence and the presence of 0.5 mM, 1.5 mM, 3 mM and 5 mM of (HDIP1 and HDIP2) inhibitors. Following the Fig. 5 increasing the inhibitor concentration the impedance as well as the inhibition efficiency of LAS also increases. Both impedance plots for HDIP inhibitors were observed to be similar. In EIS measurement charge transfer resistance ( $R_{ct}$ ) is definitely correlated to corrosion current density describe the corrosion phenomenon in the form of charge transfer controlled mechanism [33].

In order to get a more precise fit of these experimental data the EIS spectra for inhibitors (HDIP1 and HDIP2) in the form of equivalent circuit diagram shown in Fig. 6, illustrate an accurate fit with the present model achieved for all experimental outcomes. Inner part of capacitive loop alongside the real axis represents the ohmic resistance (Rs) of the adsorbed layer of the corrosion products [34]. However,

 $R_{ct}$  denote charge transfer resistance express the transfer of electrons across the surface and is inversely proportional to corrosion rate [35]. For a more accurate fit constant phase element (CPE) is replaced by double layer capacitance ( $C_{dl}$ ) in the equivalent circuit [36].

Mathematically, the impedance CPE is given by the relation [37]:

$$Z_{CPE} = Q^{-1} (j\omega)^{-n} \tag{6}$$

Where Q represents the magnitude of the CPE, j is the imaginary unit,  $\omega$  is the angular frequency



**Figure 5.** Nyquist plot for the dissolution of LAS in 1 M HCl solution without and with Quinazoline Schiff Bases concentration at 298 K.

 $(\omega = 2\pi f)$ , the frequency in Hz), and n represent the CPE component and termed as phase shift representing the extent of surface inhomogeneity. Depending on the values of the degree of component, when n = 0, CPE may be resistance R, if n is close to unity, in this case phase angle is not of 90°, where n= 1, represent the impedance of a capacitor, where Q = C<sub>dl</sub> [38].

Fig. 5 represent a single capacitive semicircle at a region of higher frequencies in both inhibited and uninhibited solutions for one time constant, indicating the corrosion of LAS in 1 M HCl media is predominantly controlled by the process of charge transfer [39, 40]. However, the deviation from the ideal semicircle appearance is usually accredited to the frequency dispersion interfacial impedance when 0.5 < n < 1. The consequences of the frequency distribution lead the surface inhomogeneities, impurities, and surface roughness, adsorption of the inhibitor and the establishment of porous layers [41, 42]. For a circuit including CPE the correction of the double layer capacitance C<sub>dl</sub> using the relation [43]:

Int. J. Electrochem. Sci., Vol. 13, 2018

$$C_{dl} = Y_o (\lambda_{max})^{n-1} \tag{7}$$

Where  $\lambda_{max}$  denote the frequency at which the imaginary part of the impedance is utmost. Different corrosion parameters including constant phase element (CPE), double layer capacitance (C<sub>dl</sub>), charge transfer resistance (R<sub>ct</sub>) and solution resistance (R<sub>s</sub>) for different concentrations of HDIP inhibitors derived from EIS measurements are enlisted in Table 4.

**Table 4.** Parameters measured by EIS method for LAS in 1 M HCl solution without and with Quinazoline Schiff Bases concentration at 298 K.

Inhibitors	Concentration	Rs		C <sub>dl</sub>	Yo		IE <sub>EIS</sub>
	(mM)	$(\Omega.cm^2)$	$R_{ct} (\Omega.cm^2)$	$(\mu F \text{ cm}^{-2})$	$(n\Omega^{-1} S^n cm^{-2})$	n	(%)
Blank		0.903	21.5	310.6	460.5	0.921	
HDIP1	0.5	1.164	64.8	53.4	83.9	0.92	64.2
	1.5	1.177	79.8	52.2	82.7	0.916	67.1
	3	0.812	121.1	51	81.6	0.901	82.3
	5	0.771	145.9	50.1	80.3	0.9	87.6
HDIP2	0.5	1.352	62.7	51.2	82.3	0.91	63.1
	1.5	1.517	76.8	49.8	80.7	0.904	64.8
	3	0.688	109.7	48.3	79.6	0.9	79.7
	5	0.651	135.3	47.5	79.1	0.902	84.5

From Table 4 it is clear that the obtained values for  $R_s$  are very small as compared to the values of  $R_{ct}$ . This behavior obviously reflects that by increasing the inhibitors concentrations and increase in  $R_s$  values and alternatively a net decrease in  $C_{dl}$  values were observed. Furthermore, the decrease in  $C_{dl}$ values result a corresponding increase in the double layer thickness and/or decrease in local dielectric constant suggested the ability of the inhibitors molecules to hinder the metal corrosion by the virtue of adsorption at metal/solution interface [43, 44]. However, lower capacitance values may affect the replacement of water molecules to a large extend due to the absorbance of inhibitor molecules at electrode surface [45]. Increasing the inhibitor concentration increases the thickness of the protective layer at the interface consequence a significant decrease in  $C_{dl}$  values.



Figure 6. Equivalent circuit diagram for fitting EIS data for LAS in 1 M HCl solution.

Fig. 6 represent an equivalent circuit diagram to model LAS/HCl interface which constitute of an  $R_{ct}$ , CPE and solution resistance  $R_s$ , where *n* stand for the phase shift which may be further attributed to the degree of surface inhomogeneities [45]. All the obtained fitted parameters are listed in Table 5.

Inhibitors	Kads (M <sup>-1</sup> )	Slop	ΔG <sup>0</sup> ads (kJmol <sup>-1</sup> )	<b>R</b> <sup>2</sup>
HDIP1	16.23x103	-1.2889	-43.42	0.9936
HDIP2	14.02x103	-1.2284	-42.87	0.9902

**Table 5.** Thermodynamic adsorption parameters for Quinazoline Schiff Bases at the optimumconcentration of LAS surface immersed in 1 M HCl at 298 K.

#### 3.5 Schiff Bases as potential corrosion inhibitors

Literature review reveals that the Schiff bases are effective corrosion inhibitors for different metals and alloys in acidic environments. Table 6 briefly summarize the selection of Schiff Bases as excellent corrosion inhibitors on the basis of their molecular structure in different acidic medium and for different metal.

Inhibition mechanism process of the corrosion inhibitors strongly depends on the adsorption mechanism governed by the several factors including the chemical structure of inhibitors. The essential aspect of the Schiff Bases as corrosion inhibitors are the existence of C=N group, pi electrons in the aromatic rings, various functional groups as well as interaction mechanism with metal surface. Insight Table 6, it was confirmed that the presence of various functional groups including: -CH<sub>3</sub>, -OH, phenyl, benzene and SH groups at different orientation are responsible for efficient adsorption. The investigated Schiff Bases in the present study consists of two to three benzene ring, one to two C=N groups. In addition, DHIP1 have two OH groups in the ortho position at two separate benzene rings and DHIP2 have one OH group in the para position of the benzene ring linked to the carbon of C=N group. Therefore the inhibition efficiency of HDIP1 is greater than HDIP2 at a common concentration of 5 mM at 25 °C. These broadly de-localized pi-electrons and cause a flat orientation of inhibitor molecules leading to higher extend of adsorption on metal surface as compared to other compounds.

**Table 6.** Schiff Bases compounds as inhibition efficiency for different metals and alloys in acidic medium.

Schiff Bases	Structure	Substrate	Medium	Efficiency	Refer
				(%)	ences
N,N <sup>/</sup> -ethylen-bis (salicylidenimine)	CH=N(CH <sub>2</sub> ) <sub>2</sub> N=HC OH HO.	Copper	0.5 M H <sub>2</sub> SO <sub>4</sub>	78	[46]

benzylidene-(2-methoxy-	1	Aluminum	1 M HCl	99.8	[47]
phenyl)-amine (A)	Ĩ <sup>™</sup>				
	N				
	(A)				
(2 mothery phonyl) (1					
(2-metholy-phenyl)-(4- methyl-benzyli-dene)-		Aluminum	1 M HCl	98.43	
amine (B)			1 1/1 1/01	,	
	К СН3				
	(B)				
[(2-pyridin-4-	2 ОН	Steel	0.5 M	78	[48]
ylethyl)thiojacetic acid	ss		HaSO		
	N O		112004		
3-(5-methoxy-2-	O OH	Mild Steel	I M HCl	93	[49]
hydroxybenzylideneamino )- $2$ -(- $5$ -methoxy- $2$ -					
hydroxyphenyl)-2,3-	NO2				
dihydroquinazoline-4(1H)-	н				
one	но				
	О он				
3-(5-nitro-2-		Mild Steel	I M HCl	90.2	
hydroxybenzylidenea	N OCH3				
mino)-2(5-nitro-2-	N OCH3				
dihydroguinazoline-4(1H)-	Н				
one					
N-[(E)-1-(2-		304 SS	1 M HCl	94.1	[50]
thienyl)methylidene]-N-(4-					
{[(Z)-1-(2 thienyl)-	s s				
l)amine					
N-[(Z)-1-(2-		304 SS	1 M HCl	90.4	
thienyl)methylidene]- $N-[4-(4-\{[(7)-1-(2-thienyl)])$					
methylidene] amino}					
benzyl)phenyl]amine					
2-((pyridin-2-	он	Carbon	1 M HCl	93.6	[51]
ymmno)metnyi)phenoi		Steel			
	≪ У—сн=м—∢ ≥	20001			
				95 /	
				<i>7</i> <b>.</b> +	
2-((hexadecylimi-					
no)methyl)phenol					



	он /	Carbon			
	СН=N-СН4(СН2)14СН3	Steel			
(E)-2-(1-(2- hydroxyethyamino)ethylmi no)ethy)phenol	HaC OH OH OH	Iron	2 M HCl	79	[52]
2,2'-(1E,1'E)-1.1'-(2,2'- azanedilbis(ethane-2.1- diyl)bis(azan-1-yl-1- ylidene))bis(ethane-1-yl-1- ylidene)		Iron	2 M HCl	88	
N ,N -bis(salicylidene)-2- hydroxy-1,3- propanediamine		Steel	5% HCl	91	[53]
N ,N -bis(2- hydroxyacetophenylidene) -2-hydroxy-1,3- propanediamine		Steel	5% HCl	94.8	
2-((1E)-2-aza-2-	S N	Carbon	0.1 M	57.4	[54]
thiophene		Steel	HCl		
2-((1Z)-1-aza-2-(2-				71.8	
pyridyl)vinyl)pyrimidine		Carbon	0.1 M		
		Steel	HCl		

# 3.6 Adsorption isotherm

Generally the efficiency of Quinazoline Schiff Bases molecules as effective corrosion inhibitors strongly depends on their adsorption tendency on metal surface. To understand the mechanism of adsorption, the adsorption of the investigated organic inhibitors at the interface may be explained by a general reaction involving a substitution process for adsorption of inhibitor molecules on metal/solution interface [55].

 $O.I_{(solution)} + X H_2O_{(adsorbed)} \longrightarrow O.I_{(adsorbed)} + X H_2O_{(solution)}$ 

Where, X represents the number of water molecules alternatively replaced by the single molecules of organic inhibitor adsorbate. In a similar fashion, O.I (solution) and O.I (adsorbed) are the organic inhibitor molecules present in the solution and adsorbed on the metal surface replacing a single water molecule, respectively. It is important to understand the type of adsorption as well as adsorption isotherm that can result as essential information during the interaction of inhibitor molecules and the corresponding active sites on metal surface. Several attempts were made to fit surface coverage ( $\theta$ ) values to the standard isotherms like Langmuir, Temkin, Freundlich Fumkin and Floy Huggins [56, 57]. Fig. 7 represent graph between (C) and (C/ $\theta$ ) produce a straight line which establish Langmuir model and can be expressed by the following relation [58]:



**Figure 7.** Langmuir adsorption isotherm of Quinazoline Schiff Base inhibitors on the surface of LAS in 1 M HCl solution

Where  $K_{ads}$  is the equilibrium constant for adsorption model and C represent the inhibitor concentration. The standard adsorption energy ( $\Delta G^o{}_{ads}$ ) of the inhibitor on the LAS surface can

be achieved from the equation [59]:

$$\Delta G_{ads}^o = -RTln(55.5 K_{ads}) \tag{9}$$

The adsorption energy with a negative sign designates spontaneous adsorption process reflecting a durable interaction of the inhibitor molecules and surrounding metal surface [60]. It is usually recognized the values of adsorption energy around of less than -20 kJmol<sup>-1</sup> are reliable for a physical adsorption, while those values around or higher than -40 kJmol<sup>-1</sup> are associated with chemisorption producing a strong covalent bond as compared to the former one [61]. In the present research work the calculated values of  $\Delta G^{\circ}$  for both HDIP1 and HDIP2 are greater than -40 kJmol<sup>-1</sup> indicating a chemical

adsorption process establishing a coordinate bond between the molecules of the investigated inhibitors and the surrounding d-orbit of the LAS surface by the virtue of the lone pair of electrons.

# 3.7 SEM analysis

SEM surface morphology was generally adopted in order to establish a connection between the selected parameters during the experiment and the morphology of the LAS substrate using scanning electron microscopy. Fig. 8 shows a damaged rough surface of LAS in the absence of inhibitor containing 1 M HCl solution over a time period of 6 h. The photomicrographs of LAS in the presence of inhibitor (see Fig. 8) clearly the evidence of a smooth surface in which the damaging effect are effectively minimized. The formation of such a smooth surface is the consequences of adsorption of inhibitors molecules on the active sites of the surface to form a protective layer at the metal/solution interface and hence reduced the corrosion rate.



**Figure 8.** SEM images for LAS (a) exposed to 1 M HCl solution (b) exposed to 1 M HCl solution containing 5 mM of both Quinazoline Schiff Bases.

# 4. CONCLUSIONS

Results obtained from the present research work following conclusions have been achieved: (1) the obtained results from weight loss, electrochemical and SEM methods revealed that both HDIP1 and HDIP2 are excellent corrosion inhibitors in HCl medium. (2) Polarization measurements revealed that the investigated inhibitors are mixed type inhibitors. (3) Inhibition efficiencies increases with increasing inhibitor concentration. Moreover, inhibition efficiencies strongly dependent parameters including: concentration, solution temperature and the structure of the investigated inhibitors. (4) The obtained values for double layer capacitance have exhibit a tendency to decrease and cause a decrease in local dielectric constant and/or an increase in thickness of the electrical double layer. (5) Adsorption of investigated Schiff Bases on LAS surface followed by Langmuir adsorption isotherm and graded as

chemical adsorption. (6) The adsorption of the Quinazoline Schiff Bases are spontaneous and exothermic in nature.

## References

- 1. E.S. Sherif, R. Erasmus, and J.Comins., J. Coll. & Interface. Sci., 309 (2) (2007) 470.
- 2. E. Sherif, and S. M. Park., *Electrochim. Acta.*, 51 (28) (2006) 6556.
- 3. G. Khan, W. J. Basirun, S. N. Kazi, P. Ahmed, L. Magaji, S. M. Ahmed, M. A. Rehman., J. Coll. & Interface. Sci., (2017) 502.
- 4. M. Ehteshamzade, T. Shahrabi, and M. Hosseini., App. Surf. Sci., 252 (8) (2006) 2949.
- 5. H. Ashassi-Sorkhabi, B. Shabani, B. Aligholipour, and D. Seifzadeh., *App. Surf. Sci.*, 252 (12) (2006) 4039.
- 6. J. Talati, J, M. Desai, and N. Shah, Mat. Chem. & Phy., 93(1) (2005) 54.
- 7. M. Bouklah, A. Ouassini, B. Hammouti, and A. El Idrissi., App. Surf. Sci., (2005) 250 (1-4) 50.
- 8. L. Faraj, and G. Khan., Int. J. Electrochem. Sci., 10 (2015) 6120.
- 9. M. Abdallah, H. Megahed, and M. Sobhi., Monatshefte für Chemie-Che., 141(12) (2010) 1287.
- 10. M. Desai, M. Desai, C. Shah, S. Desai., Corros. Sci., 26(10) (1986) 827.
- 11. R. Prabhu, T. Venkatesha, A. Shanbhag, G. Kulkarni, and R. Kalkhambkar., *Corros. Sci.*, 50 (12) (2008) 3356.
- 12. F. Liu, M. Du, J. Zhang, and M. Qiu., Corros. Sci. 51 (10) (2009) 102.
- 13. M. Elmorsi, and A. Hassanein., Corros. Sci., 41(12) (1999) 1337.
- 14. Wang, H.-L., Fan, H.-B., and Zheng, J. S., Mat. Chem. & Phy., 77(3) (2003) 655.
- 15. J. Aljourani, K. Raeissi, and M. Golozar., Corros. Sci., 51 (8) (2009) 1836.
- K. Alaoui, R. Touir, M. Galai, H. Serrar, M. Ouakki, Y. Kaya, El Kacimi., J. Bio & Tribo Corros. 4 (3) (2018). 37.
- 17. S. K. Shukla, and M.A. Quraishi., J. App. Polymer Sci., 124(6) (2012) 5130.
- RA. Prabhu, TV. Venkatesha, AV. Shanbhag, GM. Kulkarni, and RG. Kalkhambkar., *Corros. Sci.*50 (12) (2008) 3356.
- 19. A. Bousskri, A. Anejjar, H. Lgaz, M. Belkhaouda, S. Jodeh, and B. Hammouti., A. J. Env. Eng. Sci. 1(1) (2015) 2019.
- 20. F. Liu, M. Du, J. Zhang, and M. Qiu., Corros. Sci. 51 (1) (2009) 102.
- 21. A. Hermas, and M. Morad., Corros. Sci. 50 (9) (2008) 2710.
- 22. E.S.M. Sherif, R. Erasmus, and J. Comins., J. Coll. & Interface. Sci., 302 (9) (2007) 470.
- 23. G. Moretti, and F. Guidi., Corros. Sci. 44 (9) (2002).
- 24. P. Okafor, M.E. Ikpi, I. Uwah, R. Ebenso, U. Ekpe, and S. Umoren., *Corros. Sci.*, 50 (8) (2008)2310
- 25. L.G. Da Trindade, and R.S. Goncalves., Corros. Sci., 51 (8) (2009) 1578.
- 26. F.S. De Souza, and A. Spinelli., Corros. Sci., 51 (3) (2009) 642.
- 27. I. Obot, S. Umoren, and A. Johnson., J. Mater. Environ. Sci., 4(6) (2013) 1013.
- 28. H. Lgaz, R. Salghi, M. Larouj, M., Elfaydy, S. Jodeh, Z. Rouifi, Z, H. Oudda., J. Mat. & Env. Sci.,7(12) (2016) 4471.
- 29. H. Lgaz, M. Saadouni, R. Salghi, S. Jodeh, M. Elfaydy, B. Lakhrissi, H. Oudda., *Der Pharm.Lett.*, 8 (2016) 158.
- 30. H. Lgaz, R. Salghi, and I. H. Ali., Int. J. Electrochem. Sci., 13 (2018) 250.
- 31. O.L. Riggs Jr, and C. Nathan., Corros. Inhib., (1973) CC Nathan, Houston, TX.
- 32. E. Elmorsi, and A. Hassanein., Corros. Sci., 41 (12) (1999) 2337.
- 33. E. Oguzie, Y. Li, and F. Wang., J. Coll. & Interface. Sci., 310 (1) (2007) 90.
- 34. H.H. Hassan, E. Abdelghani, and M.A. Amin., Electrochim. Acta., 52 (22) (2007) 6359
- A. Abdel-Gaber, B. Abd-El-Nabey, I. Sidahmed, A. El-Zayady, and M. Saadawy., *Corros. Sci.*,48 (9) (2006) 2765.

- 36. J. De Wit, and H. Lenderink., Electrochim. Acta., 41 (7) (1996) 1111.
- 37. C. Jeyaprabha, S. Sathiyanarayanan, and G. Venkatachari., Appl. Sur. Sci., 253(2) (2006) 432.
- 38. C. Jeyaprabha, S. Sathiyanarayanan, and G. Venkatachari., Appl. Sur. Sci., 253 (2) (2006) 432.
- 39. H. Ashassi-Sorkhabi, B. Shaabani, and D. Seifzadeh., Appl. Sur. Sci., 239 (2) (2005) 154.
- 40. G. Banerjee, and SN. Malhotra., Corros. 48 (1) (1992) 10.
- 41. E. Navarro-Flores, Z. Chong, and S. Omanovic., J. Mol. Cataly. A: Chem., 226 (2) (2005) 179.
- 42. P. Okafor, C. Liu, X. Liu, Y. Zheng, F. Wang, and C. Liu., J. Sol. Stat. Electrochim., 14 (8) (2010) 1367.
- 43. E. Machnikova, K.H. Whitmire, and N. Hackerman., *Electrochim Acta.*, 53 (20) (2008) 6024.
- 44. E. Oguzie, Y.Li, and F. Wang., *Electrochim Acta.*, 53 (2) (2007) 909.
- 45. K. Khaled., *Electrochim Acta.*, 53 (9) (2008) 3484.
- 46. M. Ehteshamzade, T. Shahrabi, M.G. Hosseini., App.surf. Sci., 252 (2006) 2949.
- 47. H. Ashassi-sorkhabi, B. Shabani, B. Aligholipour, D. Seifzadeh., App. Surf. Sci., 252 (2006) 4039.
- 48. M. Boulkah, A. Quassini, B. Hammouti, A. El Idrrisi., App. Surf. Sci. 250 (2005) 50.
- 49. G. Khan, W. J. Basirun, S. N. Kazi, P. Ahmed, L. Magaji, S. M. Ahmed, M. A. Rehman, M. A., *J. Colloid. & Inter. Sci.*, 502 (2017) 134.
- 50. M. Behpour, S.M. Ghoreishi, N. Soltani, M. Salawati-Niasari., Corros. Sci. 51 (2009) 1073.
- 51. M.A. Hegazi., Corros. Sci., 51 (2009) 2610.
- 52. Ju. Hong, Kai. Zhen-Peng, Li. Yan., Corros. Sci., 50 (2008) 865.
- 53. K.C. Emergul, A.A. Akay, O. Atakol., Mat. Chem. & Phy., 93 (2005) 325.
- 54. A. Yurt, A. Balanban, U.S. Kandemir, B. Bereket, B. Erk., Mat. Chem. & Phy., 85 (2004) 420.
- 55. I. Lukovits, E. Kalman, F. Zucchi., Corros., 57 (2001) 3.
- 56. I. Obot, and N.Obi-Egbedi., J. of Chem., 7(3) (2010) 837.
- 57. A. Abdel-Gaber, B. Abd-El-Nabey, I. Sidahmed, A. El-Zayady, and M. Saadawy., *Corros. Sci.*,48(9) (2006) 2765.
- 58. H. Ashassi-Sorkhabi, M. Majidi, and K. Seyyedi., App. Sur. Sci., 225 (1) (2004) 176.
- 59. D. Daoud, T. Douadi, S. Issaadi, and S. Chafaa., Corros. Sci., 79 (2014) 50.
- 60. G. Avci., Mat. Chem. & Phy., 112(1) (2008) 234.
- 61. E. Bayol, A. Gürten, M. Dursun, and K. Kayakirilmaz., *Acta Physico-Chimica Sinica* 24(12) (2008) 2236.

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