PHYSICOCHEMICAL PROBLEMS OF MATERIALS PROTECTION

# Some Schiff Base Compounds as Inhibitors for Corrosion of Carbon Steel in Acidic Media<sup>1</sup>

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**Abstract**—The corrosion behavior of carbon steel in 0.5 M HCl solution in the absence and presence of new five Schiff bases of indole derivatives was investigated using electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM) and potentiodynamic polarization techniques. All the experimental results show that these Schiff bases have excellent corrosion inhibition performance. The polarization curves show that these compounds act as mixed type inhibitors. The adsorption of these Schiff bases on carbon steel surface is consistent with Langmuir adsorption isotherm. The effect of temperature on the rate of corrosion in the absence and presence of these compounds were also studied. Some thermodynamic functions were computed and discussed. The results obtained by the three different electrochemical techniques were in good agreement.

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## **1. INTRODUCTION**

Carbon steel is widely used as constructional material in many industries due to its excellent mechanical properties and low cost. The highly corrosive nature of aqueous mineral acids on most metals requires degree of restraint to achieve economic maintenance and operation of equipment, minimum loss of chemical product and maximum safety condition. Organic compounds containing nitrogen atoms are commonly used to reduce the corrosion attack on steel in acidic media [1-15]. Generally, the heterogeneous organic compounds having higher basicity and electron density on the hetero atoms like N, O, S have tendency to resist corrosion. Nitrogen and oxygen are the active centers for the process of adsorption on the metal surface. These compounds can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion attack. The efficiency of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pair present, the  $\pi$ orbital character of free electrons [16] and the electron density around nitrogen and oxygen atoms.

In the present investigation the inhibition efficiency of five Schiff bases viz. (E)-2-(2-phenylhydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile, (E)-2-(2-p-tolylhydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile, E)-2-(2-(4-methoxyphenyl)hydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile, (E)-2-(2-(4-chlorophenyl)hydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile and (E)-2-(2-(4-nitrophe-

nyl)hydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile have been investigated for carbon steel in HCl solution.

# 2. EXPERIMENTAL

Carbon steel of chemical composition 0.2%C, 0.35% Mn, 0.024% P, 0.003% Si, and the remainder iron Electrochemical experiments were performed in a conventional three-electrode assembly with carbon steel specimen as working electrode, saturated calomel electrode (SCE) as a reference electrode and a platinum foil  $(1.0 \text{ cm}^2)$  as a counter electrode. The reference electrode was connected to a Luggin capillary and the tip of the Luggin capillary is made very close to the surface of the working electrode to minimize IR drop. The cell was open to air and the measurement was conducted at room temperature. Tafel polarization curves were obtained by changing the electrode potential automatically from  $(-800 \text{ to } 500 \text{ mV}_{SCE})$  at open circuit potential with a scan rate of 5  $mVs^{-1}$ . Stern-Geary method [17] used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines of charge transfer controlled corrosion reactions to a point which gives  $\log i_{\rm corr}$  and the corresponding corrosion potential  $(E_{\rm corr})$  for inhibitor free acid and for each concentration of inhibitor. Then  $i_{corr}$  was used for calculation of inhibition efficiency and surface coverage ( $\theta$ ) as below:

$$\%$$
IE =  $(1 - [i_{corr(inh)}/i_{corr(free)}]) \times 100,$  (1)

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Fig. 1. Potentiodynamic polarization curves for carbon steel in 0.5 M HCl in the absence and presence of different concentrations of compound (1) at  $30^{\circ}$ C.

$$\theta = 1 - [i_{\text{corr(inh)}} / i_{\text{corr(free)}}], \qquad (2)$$

where  $i_{\text{corr(free)}}$  and  $i_{\text{corr(inh)}}$  are the corrosion current densities in the absence and presence of inhibitor, respectively.

Impedance measurements were carried out in frequency range from  $10^5$  Hz to 0.5 Hz with amplitude of 5 mV peak-to-peak using ac signals at open circuit potential. The experimental impedance were analyzed and interpreted on the basis of the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer  $R_{ct}$  (diameter of high frequency loop) and the capacity of double layer  $C_{dl}$  which is defined as:

$$C_{\rm d1} = 1/(2\pi f_{\rm max} R_{\rm ct}).$$
 (3)

The inhibition efficiencies and the surface coverage  $(\theta)$  obtained from the impedance measurements are defined by the following relations:

$$\% IE = (1 - [R_{ct}^{\circ}/R_{ct}]) \times 100, \qquad (4)$$

$$\theta = 1 - [R_{\rm ct}^{\circ}/R_{\rm ct}], \qquad (5)$$

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

Electrochemical frequency modulation, EFM, was carried out using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1 s. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. The Intermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density  $(i_{corr})$ , the Tafel slopes ( $\beta_c$  and  $\beta_a$ ) and the causality factors CF2& CF3 [18, 19].

The electrode potential was allowed to stabilize 30 min before starting the measurements. All the experiments were conducted at  $30 \pm 1^{\circ}$ C. Measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry framework system based on the ESA 400. Gamry applications include dc105 for dc corrosion measurements, EIS300 for electrochemical impedance spectroscopy and EFM 140 for electrochemical frequency modulation measurements along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing, and fitting data.

## 3. RESULTS AND DISCUSSION

#### 3.1. Tafel Polarization Study

The potentiodynamic polarization curves for carbon steel in 0.5 M HCl solutions containing different concentrations of compound (1) at 30°C are shown in Fig. 1. Similar curves were obtained for other compounds (not shown). The intersection of Tafel regions of cathodic and anodic branches gives the corrosion current density  $(i_{corr})$  and the corrosion potential  $(E_{corr})$ . Inspection of Fig. 1 revealed that addition of these compounds causes a decrease in the corrosion rate. That is, shifts both the anodic and cathodic curves to lower values of current densities. This implies that both the hydrogen evolution and anodic carbon steel dissolution reactions are inhibited. This may be ascribed to adsorption of these compounds over the corroding surface [20]. Table 2 shows the electrochemical parameters (corrosion potential,  $E_{corr}$ , anodic and cathodic Tafel slopes,  $\beta_a$ ,  $\hat{\beta}_c$ , and corrosion current density,  $i_{corr}$ ,) obtained from Tafel plots for the carbon steel electrode in 0.5 M HCl solution without and with different concentrations of investigated compounds. The results in this Table indicate that corrosion current density decreases in the presence of these compounds compared to the blank solution and also decreases with increasing concentration of the inhibitor. It is also observed that the presence of these compounds does not shift  $E_{\rm corr}$  remarkably; therefore these compounds could be regarded as mixed-type inhibitors. However, according to Ferreira and others [21, 22] if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of uninhibited solution, the inhibitor can be seen as a cathodic or anodic type. In the present study, maximum displacement was 61 mV, indicating that these compounds belonged to mixed-type. These results suggest that investigated inhibitors were first adsorbed onto the metal surface and impeded by merely blocking the metal surface without affecting the anodic and cathodic reaction mechanism [23]. The obtained efficiencies indicate these investigated compounds act as

Comp.	Structure & Names	Molecular weight & Chemical formula
1	(E)-2-(2-phenylhydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile	C <sub>17</sub> H <sub>12</sub> N <sub>4</sub> O 288.3
2	(E)-2-(2-p-tolylhydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O 302.33
3	(E)-2-(2-(4-methoxyphenyl)hydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> 318.33
4	(E)-2-(2-(4-chlorophenyl)hydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile	C <sub>17</sub> H <sub>11</sub> ClN <sub>4</sub> O 322.75
5	(E)-2-(2-(4-nitrophenyl)hydrazono)-3-(1H-indol-3-yl)-3-oxopropanenitrile	C <sub>17</sub> H <sub>11</sub> N <sub>5</sub> O <sub>3</sub> 333.3

Table 1. Molecular structures & Names of the investigated compounds are:

effective inhibitors. The order of decreasing inhibition efficiency of the investigated compounds was found to be: 1 > 2 > 3 > 4 > 5.

## 3.2. Electrochemical Impedance Spectroscopy (EIS)

The effect of inhibitor concentration on the impedance behavior of carbon steel in 0.5 M HCl solution at  $30^{\circ}$ C is presented in Fig. 2a. The curves show a similar type of Nyquist plots for carbon steel in the presence of various concentrations of compound (1). Similar curves were obtained for other compounds

(not shown). The existence of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. Deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, and formation of porous layers and inhomogenates of the electrode surface [24, 25]. Inspections of the data reveal that each impedance diagram consists of a large capacitive loop with one capacitive time constant in the Bode -phase plots (Fig. 2b). The



Fig. 2a. Nyquist plots recorded for carbon steel in 0.5 M HCl solutions without and with various concentrations of compound (1) at the respective corrosion potentials and  $30^{\circ}$ C.

**Fig. 2**b. Bode plots recorded for carbon steel in 0.5M HCl solutions without and with various concentrations of compound (1) at the respective corrosion potentials and 30°C.



**Fig. 3.** Electrical equivalent circuit used to fit the impedance data.

electrical equivalent circuit model shown in Fig. 3 was used to analyze the obtained impedance data. The model consists of the solution resistance  $(R_s)$ , the charge-transfer resistance of the interfacial corrosion reaction  $(R_{ct})$  and the double layer capacitance  $(C_{dl})$ . Excellent fit with this model was obtained with our experimental data. EIS data (Table 3) show that the  $R_{ct}$ values increases and the  $C_{dl}$  values decreases with increasing the inhibitor concentrations. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, decreasing the extent of dissolution reaction. The high  $(R_{ct})$  values, are generally associated with slower corroding system [26, 27]. The decrease in the  $C_{dl}$  can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [28], suggested that the inhibitor molecules function by adsorption at the metal/solution interface. The % IE obtained from EIS measurements are close to those deduced from polarization measurements. The order of inhibition efficiency obtained from EIS measurements is as follows: 1 > 2 > 3 > 4 > 5.

## 3.3. Electrochemical Frequency Modulation Measurements (EFM)

The EFM is a nondestructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Like EIS, it is a small ac signal. Intermodulation spectra obtained from EFM measurements are presented in Figs. 4a–4f are examples of carbon steel in 0.5 M HCl solutions devoid of and containing different concentrations of compound (1) at 30°C. Similar intermodulation spectra were obtained for other compounds (not shown). Each spectrum is a current response as a function of frequency. The calculated corrosion kinetic parameters at different concentrations of the investigated compounds in 0.5 M HCl at 30°C ( $i_{corr}$ ,  $\beta_a$ ,  $\beta_c$ , CF-2, CF-3 and % IE) are given in Table 4.

From Table 4, the corrosion current densities decrease by increasing the concentration of investigated compounds and the inhibition efficiencies increase by increasing investigated concentration of the investigated compounds. The causality factors in Table 4 are very close to theoretical values which according to EFM theory [29] should guarantee the validity of Tafel slopes and corrosion current densities. Values of causality factors in Table 4 indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The deviation of causality factors from their ideal values might due to that the perturbation amplitude was too small or that the resolution of the frequency spectrum is not high enough also another possible explanation that the inhibitor is not performing very well. The obtained results showed good agreement of corrosion kinetic parameters obtained with the EFM, Tafel extrapolation and EIS methods.

Figure 5 shows the inhibition efficiencies recorded for the five investigated compounds (1-5) at a concentration of  $10^{-6}$  M using the three different techniques, namely potentiodynamic; EIS and EFM. As seen from this Figure there are good agreement and similar trends. Based on these results, the electrochemical techniques of analysis appear valid for monitoring the corrosion inhibition of carbon steel in 0.5 M HCl in the absence and presence of various concentrations of investigated compounds.

**Table 2.** The effect of concentration of the investigated compounds on the free corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), Tafel slopes ( $\beta_a \& \beta_c$ ), inhibition efficiency (% IE), degree of surface coverage ( $\theta$ ) and corrosion rate for the corrosion of carbon steel in 0.5 M HCl at 30°C

Comp.	Conc., M	$-E_{\rm corr}$ mV, vs. SCE	$i_{\rm corr}$ , $\mu A  {\rm cm}^{-2}$	$\beta_c$ , mVdec <sup>-1</sup>	$\beta_a$ , mVdec <sup>-1</sup>	θ	% IE	C.R, $\mu m y^{-1}$
Blank	0.0	483	12.65	949	1017	_	—	146.74
	$1 \times 10^{-6}$	462	3.073	534	599	0.757	75.7	35.68
	$5 \times 10^{-6}$	456	2.418	514	569	0.809	80.9	28.05
1	$9 \times 10^{-6}$	459	2.209	521	572	0.825	82.5	25.62
	$13  imes 10^{-6}$	469	0.809	412	472	0.936	93.6	9.38
	$17 \times 10^{-6}$	471	0.743	395	457	0.941	94.1	8.62
	$21 \times 10^{-6}$	456	0.303	365	410	0.976	97.6	3.52
	$1 \times 10^{-6}$	461	3.556	604	649	0.719	71.9	41.25
	$5 \times 10^{-6}$	517	3.472	551	649	0.726	72.6	40.28
2	$9 \times 10^{-6}$	517	3.090	550	632	0.756	75.6	35.84
	$13 \times 10^{-6}$	497	2.772	540	610	0.781	78.1	32.16
	$17  imes 10^{-6}$	449	1.547	486	523	0.878	87.8	17.95
	$21 \times 10^{-6}$	481	0.794	419	478	0.937	93.7	9.21
	$1 \times 10^{-6}$	457	3.687	571	626	0.709	70.9	42.77
	$5 \times 10^{-6}$	462	3.580	558	617	0.717	71.7	41.53
3	$9 \times 10^{-6}$	451	3.257	572	609	0.743	74.3	37.78
	$13 \times 10^{-6}$	469	2.831	535	601	0.776	77.6	32.84
	$17 \times 10^{-6}$	472	2.306	513	579	0.818	81.8	26.75
	$21 \times 10^{-6}$	456	1.708	488	543	0.865	86.5	19.81
	$1 \times 10^{-6}$	482	4.139	609	681	0.673	67.3	48.01
	$5 \times 10^{-6}$	461	3.886	606	654	0.693	69.3	45.08
4	$9 \times 10^{-6}$	512	3.535	552	646	0.721	72.1	41.01
	$13 \times 10^{-6}$	451	3.257	572	609	0.743	74.3	37.78
	$17 \times 10^{-6}$	446	2.824	548	585	0.777	77.7	32.97
	$21 \times 10^{-6}$	463	2.057	504	558	0.837	83.7	23.86
	$1 \times 10^{-6}$	480	8.346	819	876	0.340	34.0	96.81
	$5 \times 10^{-6}$	480	5.733	718	760	0.547	54.7	66.50
5	$9 \times 10^{-6}$	512	4.118	598	672	0.674	67.4	47.77
	$13 \times 10^{-6}$	489	3.954	640	709	0.687	68.7	45.87
	$17 \times 10^{-6}$	496	3.323	556	631	0.737	73.7	38.55
	$21 \times 10^{-6}$	503	2.632	531	605	0.792	79.2	30.53

#### 3.4. Adsorption Isotherms

Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best description of the adsorption behavior of the investigated Schiff base compounds which obeys:

$$C_{\rm inh}/\theta = 1/K + C_{\rm inh}, \qquad (6)$$

where  $C_{\text{inh}}$  is the inhibitor concentration,  $\theta$  is the fraction of the surface coverage, *K* is the modified adsorption equilibrium constant which can be related to the free energy of adsorption  $\Delta G_{\text{ads}}^{\circ}$  and  $C_{\text{solvent}}$  is the molar

concentration of solvent which in the case of the water is 55.5 mol  $L^{-1}$  by the following equation:

$$K_{\rm ads} = 1/C_{\rm solvent} \exp[-\Delta G_{\rm ads}^{\circ}/RT].$$
(7)

Where *R* is the universal gas constant and *T* is the absolute temperature. All correlation coefficient ( $R^2$ ) exceeded 0.99 indicates that the inhibition of carbon steel by these compounds was attributed to adsorption of these compounds on the carbon steel surface. To calculate the surface coverage ( $\theta$ ), it was assumed that the inhibitor efficiency is due mainly to the blocking effect of the adsorbed species and hence % IE =  $100 \times \theta$ .

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**Figs. 4a–4f**. Intermodulation spectrum for carbon steel in 0.5 M HCl solutions without and with various concentrations of compound (1) at 30°C.



**Fig. 5.** Comparison of inhibition efficiencies (recorded using potentiodynamic, EIS and EFM measurements) for carbon steel in 0.5 M HCl solutions containing various concentrations of the investigated compounds at 30°C.

The impedance results were used to calculate the adsorption isotherm parameters. The surface coverage ( $\theta$ ) data are very useful while discussing the adsorption characteristics. The plot of  $C/\theta$  vs. C for all investigated compounds gave a straight line (Fig. 6) characteristic of the Langmuir adsorption isotherm.

The calculated  $\Delta G_{ads}^{\circ}$  values, using Eq. (7), were also given in Table (5).  $\Delta G_{ads}^{\circ}$  is expressed in kJ mol<sup>-1</sup> of Org<sub>ads</sub>. The negative values of  $\Delta G_{ads}^{\circ}$  ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface. It is well known that values of  $\Delta G_{ads}^{\circ}$  of the order of 40 kJ mol<sup>-1</sup> or higher involve charge sharing or transfer from the inhibitor molecules to metal surface to form coordinate type of bond (chemisorption); those of order of 20 kJ mol<sup>-1</sup> or lower indicate a physisorption [30–32].

The calculated  $\Delta G_{ads}$  values (Table 5) are in the range less than -40 kJ mol<sup>-1</sup> indicates, therefore, that the adsorption mechanism of the investigated compounds on carbon steel in 0.5 M HCl solution is not a simple physical adsorption but it may involve some other interactions. The higher negative values of  $\Delta G_{\rm ads}^{\circ}$ indicate that these inhibitors are strongly adsorbed on the carbon steel surface. Moreover,  $|\Delta G_{ads}^{\circ}|$  of investigated compounds decreases in the order 1 > 2 > 3 >4 > 5. This is in good agreement with the ranking of inhibitors efficiency obtained from the different investigated techniques. The high value of K for investigated compounds indicates stronger adsorption on the carbon steel surface in 0.5 M HCl solution. The strong interaction of inhibitor with carbon steel surface can be attributed to the presence of N, O atoms and  $\pi$ -electrons in the inhibitor molecules. Lagrence et al. [33] have reported that the higher K value (>100  $M^{-1}$ ), the stronger and more stable adsorbed layer is forming which results in the higher inhibition efficiency. Data in Table (2) support the good inhibition performance of investigated compounds as corrosion inhibitors for carbon steel in 0.5 M HCl solution.

## 3.5. Effect of Temperature and Activation Parameters

The dependence of corrosion current density on the temperature can be expressed by Arrhenius equation:

$$i_{\rm corr} = A \exp((-E_{\rm a}^*)/RT), \qquad (8)$$

where A is the pre-exponential factor and  $E_a^*$  is the apparent activation energy of the corrosion process. Arrhenius plot obtained for the corrosion of carbon steel in HCl solution is shown in Fig. 7 presents the Arrhenius plot in the presence of  $17 \times 10^{-6}$  M investigated compounds.  $E_a^*$  values determined from the

Comp.	Cone, M	$C_{\rm dl},\mu{\rm Fcm^{-2}}$	$R_{\rm ct}, \Omega  {\rm cm}^2$	θ	%IE
Blank	0.00	96.98	15.38	—	—
1	$1.0 \times 10^{-6}$	57.32	47.24	0.674	67.4
	$5.0  imes 10^{-6}$	60.64	118.4	0.870	87.0
	$9.0 \times 10^{-6}$	98.62	212.9	0.928	92.8
	$13.0 \times 10^{-6}$	86.95	251.7	0.939	93.9
	$21.0\times10^{-6}$	24.13	339.6	0.955	95.5
2	$1.0 \times 10^{-6}$	67.69	41.78	0.632	63.2
	$5.0 \times 10^{-6}$	79.13	70.72	0.783	78.3
	$9.0 \times 10^{-6}$	59.24	184.3	0.917	91.7
	$13.0 \times 10^{-6}$	43.28	229.1	0.933	93.3
	$21.0\times10^{-6}$	53.16	334.3	0.954	95.4
3	$1.0 \times 10^{-6}$	31.77	38.06	0.596	59.6
	$5.0  imes 10^{-6}$	32.66	53.34	0.712	71.2
	$9.0 \times 10^{-6}$	74.52	111.3	0.862	86.2
	$13.0 \times 10^{-6}$	73.39	204.1	0.925	92.5
	$21.0\times10^{-6}$	61.19	244.9	0.937	93.7
4	$1.0 \times 10^{-6}$	65.44	36.41	0.578	57.8
	$5.0 \times 10^{-6}$	43.75	50.90	0.698	69.8
	$9.0 \times 10^{-6}$	52.02	69.55	0.779	77.9
	$13.0 \times 10^{-6}$	50.08	115.7	0.867	86.7
	$21.0 \times 10^{-6}$	41.65	183.7	0.916	91.6
5	$1.0 \times 10^{-6}$	10.17	20.88	0.263	26.3
	$5.0 \times 10^{-6}$	84.24	50.88	0.698	69.8
	$9.0 \times 10^{-6}$	74.54	57.10	0.731	73.1
	$13.0 \times 10^{-6}$	84.99	87.18	0.824	82.4
	$21.0\times10^{-6}$	70.49	94.99	0.838	83.8

**Table 3.** Electrochemical kinetic parameters obtained by EIS technique for carbon steel in 0.5 M HCl solution containing various concentrations of the investigated compounds at  $30^{\circ}$ C

slopes of these linear plots are shown in Table 6. The linear regression ( $R^2$ ) is close to 1 which indicates that the corrosion of carbon steel in 0.5 M HCl solution can be elucidated using the kinetic model. Table 6 showed that the value of  $E_a^*$  for inhibited solution, suggesting that dissolution of carbon steel is slow in the presence of inhibitor and can be interpreted as due to physical adsorption [34]. It is known from Eq. 8 that the higher  $E_a^*$  values lead to the lower corrosion rate. This is due to the formation of a film on the carbon steel surface serving as an energy barrier for the carbon steel corrosion [35].

Enthalpy and entropy of activation ( $H^*$ ,  $S^*$ ) of the corrosion process were calculated from the transition state theory (Table 6):

$$Rate(i_{corr})$$
(9)  
= (*RT*/*Nh*)exp( $\Delta S^*/R$ )exp( $-\Delta H^*/RT$ ),

where h is Planck's constant and N is Avogadro's number. A plot of log  $(i_{corr}/T)$  vs. 1/T for c-steel in 0.5 M HCl at  $17 \times 10^{-6}$  M investigated compounds, gives straight lines as shown in Fig. 8. Values of  $\Delta H^*$  are positive. This indicates that the corrosion process is an endothermic one. The entropy of activation is large and negative. This implies that the activated complex represents association rather than dissociation step, indicating that a decrease in disorder takes place, going from reactants to the activated complex [36].

The order of decreasing inhibition efficiency of the investigated compounds as gathered from the increase in  $E_a^*$  and  $\Delta H^*$  values and decrease in  $\Delta S^*$  values, is as follows: 1 > 2 > 3 > 4 > 5.



**Fig. 6.** Langmuir adsorption isotherm for carbon steel in 0.5 M HCl solutions containing various concentrations of the investigated compounds from polarization study at 30°C.

#### 3.6. Mechanism of Corrosion Inhibition

From the observations drawn from the different methods, one can conclude that the inhibitor is adsorbed on carbon steel surface forming a barrier film and protect carbon steel substrate against corrosion in 0.5 M HCl solution. Their inhibitive action can be explained on the basis of the N and O atoms in addition to a  $\pi$  electron interaction of the benzene nucleus with unshared p electrons of carbon steel atoms, which contribute to the donor acceptor bond between the non bonding electron pairs and the vacant orbitals of the metal surface. As far as the inhibition process is

 $\begin{array}{c} \bullet 0.5 \ \mathrm{HCl} \ R^2 = 0.99523 \\ \bullet \ \mathrm{Compound} \ 1 \ R^2 = 0.99576 \\ \bullet \ \mathrm{Compound} \ 2 \ R^2 = 0.99434 \\ \bullet \ \mathrm{Compound} \ 3 \ R^2 = 0.99438 \\ \bullet \ \mathrm{Compound} \ 3 \ R^2 = 0.99438 \\ \bullet \ \mathrm{Compound} \ 4 \ R^2 = 0.99354 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ R^2 = 0.99485 \\ \bullet \ \mathrm{Compound} \ 5 \ \mathrm{Compound}$ 

Fig. 7. Log *i* (corrosion rate) -1/T curves for carbon steel

dissolution in 0.5 M HCl in the absence and presence of

 $17 \times 10^{-6}$  M of the investigated compounds.

concerned, it is generally assumed that adsorption of the inhibitor at the metal/solution interface is the first step in the action mechanism of the inhibitors in aggressive acid media. The adsorption may be the result of one or more of three types of interactions [37], namely; electrostatic attraction between charged molecules and charged metal, coordination of the unshared pairs of electron on the molecule to the metal atom, and involvement of  $\pi$  electrons of the inhibitor molecule in coordination process.

The inhibition efficiency is obviously dependent on the strength of adsorption and this, in term, is affected by the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and extent of formation of metallic complexes [11]. It has been known that, the number of  $\pi$  electrons in the molecule has an important role on the adsorption. It is also, accepted that  $\pi$ -electrons of double bonds in a compound can interact with metal surfaces.

It has been found that most of the organic inhibitors act by adsorption on the metal surface [9]. This phenomenon is influenced by the nature and surface charge of metal, by the type of aggressive electrolyte, and by the chemical structure of inhibitors [38].

In general, the investigated compounds may be adsorbed on carbon steel surface in their neutral or protonated forms (cationic form). Since it is well known that the carbon steel surface is positively charged in acid solution [39, 40], so, it is difficult for the protonated molecules to approach the positively charged carbon steel surface due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, thus they could growing excess negative charges in the vicinity of the interface and favor more



Fig. 8.

Comp.	Cone, M	$i_{\rm corr,}\mu{\rm Acm}^{-2}$	$-\beta_c$ , mVdec <sup>-1</sup>	$-\beta_a$ , mVdec <sup>-1</sup>	CF-2	CF-3	θ	%IE	CR, mmy <sup>-1</sup>
Blank	0.00	765.2	43	34	1.66	2.36	0.00	0.00	292.2
1	$1 \times 10^{-6}$	182.6	99	79	1.91	2.26	0.761	76.1	69.60
	$5 \times 10^{-6}$	159.1	136	95	2.02	3.03	0.792	79.2	60.63
	$9 \times 10^{-6}$	127.5	144	101	1.90	4.76	0.833	83.3	48.61
	$13 \times 10^{-6}$	115.8	134	100	2.04	2.74	0.849	84.9	44.13
	$21 \times 10^{-6}$	92.65	??	99	1.82	2.87	0.879	87.9	35.38
2	$1 \times 10^{-6}$	192.4	37	33	1.71	2.31	0.749	74.9	111.5
	$5  imes 10^{-6}$	162.4	73	33	2.18	5.13	0.788	78.8	96.37
	$9 \times 10^{-6}$	141.1	111	94	1.94	4.35	0.816	81.6	72.84
	$13 \times 10^{-6}$	129.4	168	132	1.93	2.99	0.831	83.1	60.75
	$21 \times 10^{-6}$	99.75	73	59	1.90	8.79	0.870	87.0	36.50
3	$1 \times 10^{-6}$	257.5	65	54	1.23	1.37	0.663	66.3	174.7
	$5 \times 10^{-6}$	218.9	119	100	2.04	3.92	0.714	71.4	159.7
	$9 \times 10^{-6}$	203.7	131	105	2.11	3.41	0.735	73.5	146.5
	$13 \times 10^{-6}$	193.0	146	112	1.99	2.62	0.748	74.8	115.1
_	$21 \times 10^{-6}$	177.2	226	104	2.01	3.24	0.768	76.8	105.9
4	$1 \times 10^{-6}$	311.7	88	84	685.3	1.27	0.592	59.2	195.0
	$5 \times 10^{-6}$	290.2	165	148	2.56	3.39	0.621	62.1	187.2
	$9 \times 10^{-6}$	263.1	142	117	2.08	3.36	0.656	65.6	176.5
	$13  imes 10^{-6}$	232.8	127	106	2.09	3.33	0.696	69.6	88.73
	$21 \times 10^{-6}$	203.3	123	90	2.02	3.69	0.734	73.4	58.44
5	$1 \times 10^{-6}$	364.4	190	133	2.06	3.18	0.524	52.4	253.2
	$5 \times 10^{-6}$	391.8	71	67	1.02	1.49	0.488	48.8	187.5
	$9 \times 10^{-6}$	340.8	302	42	2.33	3.17	0.555	55.5	168.0
	$13 \times 10^{-6}$	311.3	55	37	1.59	2.82	0.593	59.3	118.7
	$21 \times 10^{-6}$	258.7	113	93	2.07	2.95	0.662	66.2	60.51

**Table 4.** Electrochemical kinetic parameters obtained by EFM technique for carbon steel in 0.5 M HCl solutions containing various concentrations of the investigated compounds at  $30^{\circ}$ C

adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between positively charged molecules and the negatively charged metal surface. Thus there is a synergism between chloride ions and protonated Schiff base compounds. Thus we can conclude that inhibition of carbon steel corrosion in 0.5 M HCl is mainly due to electrostatic interaction. The decrease in inhibition efficiency with rise in temperature supports electrostatic interaction.

Inhibitors	$E_{ m a}^{st}$ , kJ mol $^{-1}$	$\Delta H^*$ , kJ mol <sup>-1</sup>	$-\Delta S^*$ , J mol <sup>-1</sup> K <sup>-1</sup>
0.5 M HCl	48.6	21.2	24.2
Compound (1)	58.7	22.3	26.3
Compound (2)	55.0	21.5	25.2
Compound (3)	53.2	21.1	24.2
Compound (4)	52.0	21.0	23.1
Compound (5)	51.7	20.6	22.8

**Table 6.** Activation parameters of the corrosion of carbon steel in 0.5 M HCl at  $10^{-4}$  M for the investigated compounds

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Inhibitors	$K \times 10^{-5},  \mathrm{M}^{-1}$	$-\Delta G_{\rm ads}^{\rm o}$ , kJ mol <sup>-1</sup>
Compound (1)	9.9	28.5
Compound (2)	6.5	27.4
Compound (3)	5.9	27.2
Compound (4)	4.7	26.6
Compound (5)	3.7	26.0

**Table 5.** Equilibrium constant and adsorption free energy of the investigated compounds adsorbed on carbon steel

## 5. CONCLUSIONS

(1) The investigated compounds are good inhibitors and act as mixed type inhibitors for carbon steel corrosion in HCl solution.

(2) The results obtained from all electrochemical measurements show that the inhibiting properties increase with inhibitor concentration. The % IE is in accordance to the order: 1 > 2 > 3 > 4 > 5 with small differences in their numerical values.

(3) Double layer capacitances decrease with respect to blank solution when the inhibitor added. This fact may explained by adsorption of the inhibitor molecule on the carbon steel surface.

(4) The adsorption of these compounds on c-steel surface in HCl solution follows Langmuir adsorption isotherm.

(5) The negative values of  $\Delta G_{ads}^{\circ}$  show the spontaneity of the adsorption.

(6) The values of inhibition efficiencies obtained from the different independent quantitative techniques used showed the validity of the results.

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