

The Inhibition of Carbon Steel Corrosion in Hydrochloric Acid Solution using Some Phenolic Compounds

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Received: 30 October 2011 / Accepted: 10 December 2011 / Published: 1 January 2012

The corrosion inhibition of carbon steel in 1.0 M hydrochloric acid solution in the presence of some phenolic compounds such as o-aminophenol, catechol, salicaldehyde and salicylic acid was investigated using weight-loss method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Results obtained showed that the inhibition efficiency of these compounds increased by increasing their concentration but decreases with a rise in temperature. The effect of the investigated compounds and KI, KSCN and KBr has also been studied. The apparent activation energy (E_a) and other thermodynamic parameters for the corrosion process have also been calculated. The potentiodynamic polarization data indicated that the inhibitors were of mixed-type. The slopes of the cathodic and anodic Tafel lines (β_c and β_a) are approximately constant and independent of the inhibitor concentration. The adsorption of these compounds on C- steel surface has been found to obey the Freundlich adsorption isotherm. Double layer capacitance, C_{dl} , and charge transfer resistance, R_{ct} , values were derived from Nyquist and Bode plots obtained from A.C. impedance studies. The mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitors.

Keywords: Corrosion inhibitors; C-steel; electrochemical impedance spectroscopy; Synergistic effect, Adsorption

1. INTRODUCTION

The development of inhibitors of steels in acid solutions has been the subject of great interest especially from the point of view of their efficiency and applications. The most important feature in C-steel is its corrosion resistance to the atmosphere and too many aqueous media due to the presence of a

rapidly formed thin and highly protective barrier oxide film that is bonded strongly to its surface, which separates the bare metal from the corrosive environment. However the presence of aggressive anions like chloride creates extensive localized attack. Its commonly states that the oxide film is stable over a pH range of about 4.5 to 8.5 [1]. Hydrochloric acid is widely used for the removal of rust and industrial acid cleaning, acid descaling and oil well acidising, because of the general aggressiveness of acid solutions, the practice of inhibition is commonly used to reduce the corrosive attack on metallic materials. Inhibitors are generally used for this purpose to control the metal dissolution.

A number of studies have recently appeared in the literature [2-10] on the topic of the corrosion of C- steel in acidic solutions. The present study aimed to investigate the efficiency of the investigated compounds as corrosion inhibitors for C- steel in acidic solutions (hydrochloric acid solution) by weight loss method, by potentiodynamic polarization method and by electrochemical impedance, the effect of addition of different salts like KI, KSCN and KBr on the corrosion inhibition of the compounds used and the effect of temperature on the rate of corrosion in order to calculate some thermodynamic parameters related to the corrosion process.

2. EXPERIMENTAL TECHNIQUES

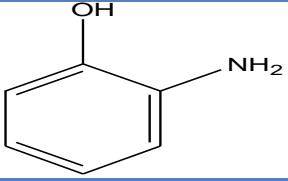
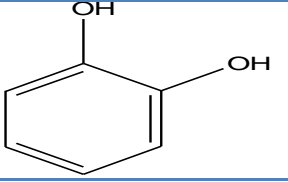
2.1. Materials

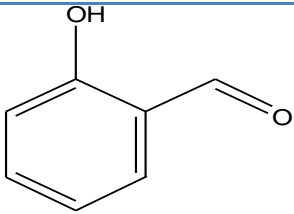
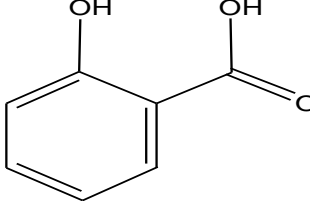
The experiments were performed with pure C- steel sheets having the chemical composition given in Table (1).

Table 1. Chemical composition of C- steel

Element	C	Mn	P	Si	Fe
Weight (%)	0.19	0.34	0.024	0.0026	99.4434

The organic inhibitors (BDH grade) used in this study were listed below and used as received.

No.	Name and Mol. Formula	Structure	Mol. Wt.
(1)	o- aminophenol C_6H_7ON		109
(2)	Catechol $C_6H_6O_2$		110

(3)	Salicaldehyde $C_7H_6O_2$		122
(4)	Salicylic acid $C_7H_6O_3$		138

2.1.1. Preparation of hydrochloric acid and inhibitors solutions

Hydrochloric acid (BDH grade) solutions were prepared by diluting the appropriate volume of the concentrated chemically pure grade acid, with double distilled water. The concentration of the acid was checked by titration of an appropriately diluted portion with standard solution of sodium carbonate. From these stocks (concentrated solutions) exactly 1 M HCl were prepared by dilution with double distilled water, which was used throughout experiments for the preparation of solutions.

100 ml stock solutions (0.1 M) of the additives (1-4) were prepared by dissolving an accurately weight quantity of each material in the appropriate volume of ethanol, then the required concentrations (1×10^{-4} – 11×10^{-4} M) were prepared by dilution with doubly distilled water.

100 ml stock solutions (1 M) of the salt (BDH grade) were prepared by dissolving an accurately weight quantity of each material in the appropriate volume of doubly distilled water, from these stock solutions exactly 1×10^{-2} M was prepared by dilution with doubly distilled water.

Three different techniques have been employed for studying the inhibition of corrosion of C-steel by these compounds these are:

- a) Chemical technique (Weight loss method).
- b) Electrochemical technique (potentiodynamic polarization method).
- c) Electrochemical impedance spectroscopy (EIS).

2.2. Chemical technique (Weight loss method)

The reaction basin used in this method was graduated glass vessel 6 cm inner diameter and having a total volume of 250 ml. 100 ml of the test solution were employed in each experiment. The test pieces were cut into 2 x 2 cm. They were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), ultrasonically degreased in alkaline degreasing mixture, rinsed in doubly distilled water and finally dried between two filter papers and weighed. The test pieces were suspended by suitable glass hooks at the edge of the basin, and under the surface of the test solution by about 1cm. After specified periods of time, the test pieces were taken out of the test solution, rinsed in doubly distilled water, dried as before and weighed again. The average weight loss at a certain time for each set of the test pieces was recorded to the nearest 0.001g.

2.3. Electrochemical technique (potentiodynamic polarization method)

Three different types of electrodes were used during polarization measurements: The working electrode was C- steel electrode, which cut from C- steel sheets. The electrodes were of dimensions 1cm x 1cm and were weld from one side to a copper wire used for electric connection. The samples were embedded in glass tube using epoxy resin. Saturated calomel electrode (SCE) and a platinum coil as reference and auxiliary electrodes, respectively, were used.

A constant quantity of the test solution (100ml) was taken in the polarization cell. A time interval of about 30 minutes was given for the system to attain a steady state. Both cathodic and anodic polarization curves were recorded galvanostatically using Potentiostat/Galvanostat (GAMRY) for calculation of electrochemical parameters and accurate measurements of potential and current density calculated using personal computer with galvanostatic polarization software. All the experiments were carried out at 30 ± 1 °C by using ultra circulating thermostat.

2.4. Electrochemical techniques (Electrochemical Impedance Spectroscopy)

The electrodes used were cut from wire of a diameter 0.6 mm. Then fixed with epoxy resin at one end into a Pyrex glass tubing of appropriate diameter leaving the exposed length, 1 cm, to contact the solution. The EIS measurements were carried out in a conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode. C- steel rod is the working electrode. The cell was kept at a constant temperature (30 ± 1 °C).

3. RESULTS AND DISCUSSION

3.1. Weight-loss measurements

Weight-loss of C- steel was determined, at various time intervals, in the absence and presence of different concentrations of the investigated compounds. The obtained corrosion rate - time curves are represented in (Fig.1) for inhibitor (1) that the most effective one. Similar curves were obtained for other inhibitors (not shown). The degree of dissolution, of course, dependent on the surface area of the metal exposed and the time of exposure; hence the amount of corrosion is given with respect to area and time. The resulting quantity, corrosion rate, is thus a fundamental measurement in corrosion science. Corrosion rates can be evaluated by measuring either the concentration of the dissolved metal in solution by chemical analysis or by measuring weight of a specimen before and after exposure and applying Eq.(1).

$$\Delta W = W_B - W_A \quad (1)$$

The percentage of inhibition efficiency (% IE) and the degree of metal surface coverage (θ) of the investigated compounds were computed by the following equations (2) & (3) respectively:

$$\% \text{ IE} = (1 - \Delta W_{\text{inh}} / \Delta W_{\text{free}}) \times 100 \tag{2}$$

$$\theta = 1 - \Delta W_{\text{inh}} / \Delta W_{\text{free}} \tag{3}$$

where ΔW_{inh} and ΔW_{free} are the weight losses of metal per unit area in the presence and absence of the inhibitors respectively at given time period and temperature.

In order to get a comparative view, the variation of the inhibition efficiency (% IE) of the investigated compounds with their molar concentrations was calculated according to Eq. (2). The values obtained are summarized in Table (2).

Careful inspection of these results showed that, at the same inhibitor concentration, the order of decreasing inhibition efficiency of the investigated compounds is as follows: 1 > 2 > 3 > 4

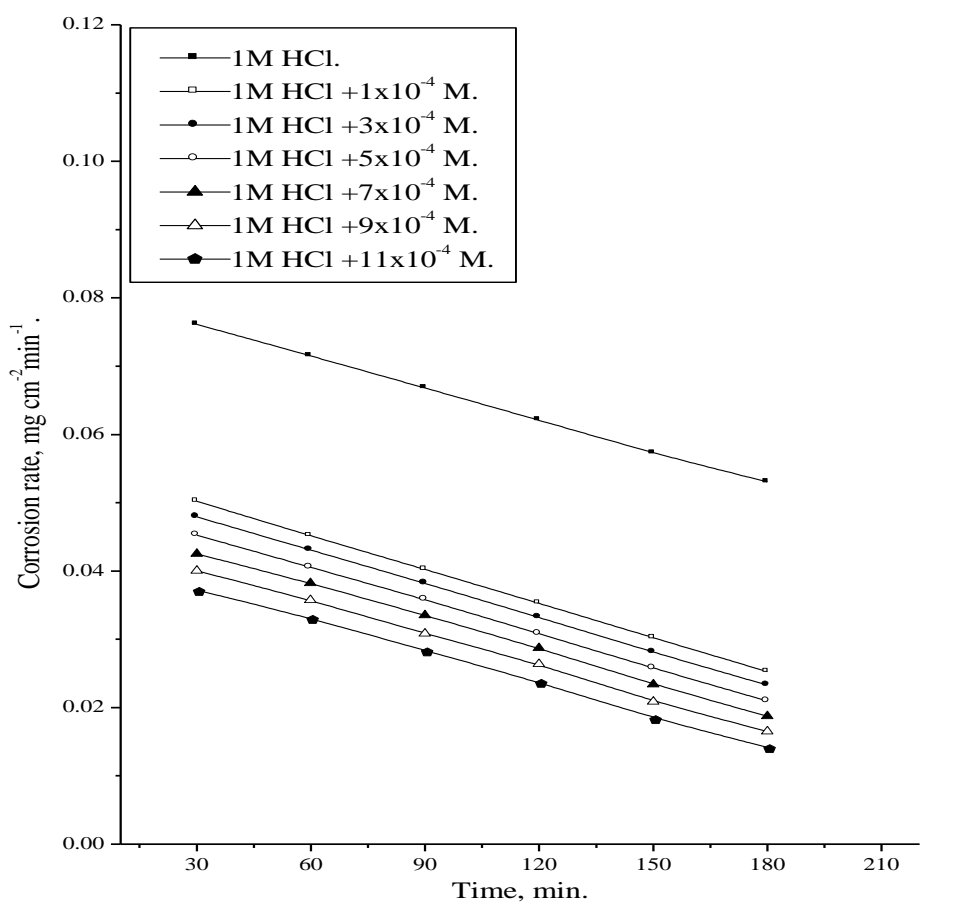


Figure 1. Corrosion rate – time curves for corrosion of C – steel in 1 M HCl in the absence and presence of different concentration of compound (1) at 30°C

3.1.1. Synergistic effect

The corrosion of C- steel in 1 M hydrochloric acid in the absence and presence of different concentrations of the investigated compounds with addition of a specific concentration (10⁻² M) of KI,

KSCN and KBr, respectively was studied. The values of inhibition efficiency (% IE) for specific concentration of KI, KSCN and KBr salts in the presence of various concentrations of inhibitors are given in Tables 3-5. From these values, it is observed that % IE of the inhibitors increases on addition of KI, KSCN and KBr salts and each anion plays a certain effect on the decreasing of corrosion rate process according to the following order: Iodide > thiocyanate > bromide. The strong chemisorption of iodide, thiocyanate and bromide ions on the metal surface is responsible for the synergistic effect of these anions in combination with cation of the inhibitor.

Table 2. Values of % inhibition efficiencies of inhibitors for the corrosion of C- steel in 1 M HCl from weight-loss measurements at different concentrations at 30 °C.

Concentration M	% IE			
	(1)	(2)	(3)	(4)
1x10 ⁻⁴	43.2	38.2	29.3	24.2
3x10 ⁻⁴	46.5	43.2	34.3	28.5
5x10 ⁻⁴	50.4	47.5	39.1	33.2
7x10 ⁻⁴	53.8	51.4	44.0	35.7
9x10 ⁻⁴	57.6	55.6	48.8	39.9
11x10 ⁻⁴	61.7	60.2	53.0	43.6

The cation is then adsorbed by columbic attraction on the metal surface where these ions are already adsorbed by chemisorption. thus, the inhibitor is not adsorbed directly on the metal surface itself, but rather by columbic attraction to the adsorbed halide ions on the metal surface. This process is similar to the so called phenomenon of anion – induced adsorption and may be represented by the highly simplified mechanism [11,12].



where X_s , M_s are the halide ion and organic species respectively in the bulk solution and X_{ads} , MX_{ads} refer to the halide ion and ion – pair respectively in the adsorbed state. This ion – pair interaction increases the surface coverage thereby reducing metal dissolution.

The order of decreasing inhibition efficiency of the investigated compounds on addition of a specific concentration of the used salts is as follow: 1 > 2 > 3 > 4

It can be seen from Tables (3-5) that the addition of a specific concentration (10⁻² M) of KI, KSCN and KBr inhibits the corrosion of C- steel in 1 M hydrochloric acid in the absence and presence of different concentrations of the investigated compounds to a large extent. This can be interpreted according to Schmitt and Bedbur [13] which proposed two types of joint adsorption namely competitive and cooperative. The synergistic inhibition effect was evaluated using a parameter, S_0 ,

obtained from the surface coverage values (θ) of the anion, cation and both. Aramiki and Hackerman [14] calculated the synergism parameter, S_0 , using the following equation.

$$S_0 = 1 - \theta_{1+2} / 1 - \theta'_{1+2} \tag{4}$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, θ_1 = surface coverage by anion, θ_2 = surface coverage by cation and θ'_{1+2} = measured surface coverage by both the anion and the cation

The value of S_0 are nearly equal to unity, which suggests that the enhanced inhibition efficiency caused by the addition of iodide, thiocyanate and bromide ions individually to the used compounds, is due mainly to the synergistic effect.

Table 3. Inhibition efficiency (% IE) at different concentrations of the inhibitors with addition of 1×10^{-2} M KI for the corrosion of C- steel after 120 minutes immersion in 1 M HCl at 30 °C.

Concentration M	% IE			
	(1)	(2)	(3)	(4)
1×10^{-4}	66.8	54.3	43.1	39.6
3×10^{-4}	71.3	59.6	48.0	43.8
5×10^{-4}	76.3	64.6	53.0	48.1
7×10^{-4}	80.8	70.4	57.6	52.7
9×10^{-4}	85.0	75.2	62.5	57.5
11×10^{-4}	88.7	80.2	67.3	61.8

Table 4. Inhibition efficiency (% IE) at different concentrations of the inhibitors with addition of 1×10^{-2} M KSCN for the corrosion of C- steel after 120 minutes immersion in 1 M HCl at 30 °C.

Concentration M	% IE			
	(1)	(2)	(3)	(4)
1×10^{-4}	57.0	46.2	39.3	34.8
3×10^{-4}	61.5	51.9	43.8	39.5
5×10^{-4}	66.5	56.0	48.1	43.8
7×10^{-4}	70.4	60.7	53.3	48.5
9×10^{-4}	75.2	65.4	58.1	53.8
11×10^{-4}	79.5	70.4	62.5	58.8

Table 5. Inhibition efficiency (% IE) at different concentrations of the inhibitors with addition of 1×10^{-2} M KBr for the corrosion of C- steel after 120 minutes immersion in 1 M HCl at 30 °C.

Concentration M	% IE			
	(1)	(2)	(3)	(4)
1×10^{-4}	52.0	41.5	32.7	28.2
3×10^{-4}	57.2	46.9	37.7	33.3
5×10^{-4}	62.2	52.5	42.7	37.7
7×10^{-4}	67.5	58.3	47.8	43.0
9×10^{-4}	72.1	63.6	53.3	47.7
11×10^{-4}	77.6	69.1	58.1	52.7

3.1.2. Adsorption Isotherm

Adsorption isotherm equations are generally of the form [15].

$$f(\theta, x) \exp(-a, \theta) = K C \quad (5)$$

where: $f(\theta, x)$ is the configurationally factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm and a is a molecular interaction parameter depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface.

From this equation. $\log \theta = \log K + n \log C$ ($0 < n < 1$)

Plots of $\log \theta$ vs. $\log C$ (Freundlich adsorption plots) for adsorption of the investigated compounds on the surface of C- steel in 1 M hydrochloric acid over the temperature range from 30 °C to 50 °C are shown in (Fig. 2) for inhibitor (1) that the most effective one. The data gave straight lines with a correlation coefficient more than 0.99, showing that the adsorption of these inhibitors in acidic solution is fitted to Freundlich adsorption isotherm. The intercept of these lines is $\log K$ and their slopes represent n . From this Figure the order of decreasing inhibition efficiency of the used compounds is as follows: $1 > 2 > 3 > 4$

All adsorption expressions include the equilibrium constant of the adsorption process, K , which is related to the standard free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) by the following equation [16-17]

$$K = 1/55.5 \exp(-\Delta G_{\text{ads}}^{\circ}/RT) \quad (6)$$

where: R is the universal gas constant, T is the absolute temperature & the value 55.5 is the concentration of water in mol/l.

The value of $\Delta G_{\text{ads}}^{\circ}$, K & n for investigated compounds in 1 M HCl solution are given in Table (6). It is clear that the value of $\Delta G_{\text{ads}}^{\circ}$ increases with the increasing solvation energy of adsorbed species which in turn increases with increasing the size of the molecule [18]. The negative sign of $\Delta G_{\text{ads}}^{\circ}$ indicates that the inhibitors are spontaneously adsorbed on the metal surface [19]. Generally, the magnitude of $\Delta G_{\text{ads}}^{\circ}$ is around to -11 kJ mol^{-1} or less negative, which can be assumed that an

electrostatic interaction exists between the inhibitor and the charged metal surface (i.e. physisorption). Standard free energy of adsorption (ΔG°_{ads}) around -40 kJ mol^{-1} or more negative indicates that a charge sharing or transferring from organic species to the metal surface occurs to form a coordinate type of bond (i.e. chemisorptions) [20-21] and vice versa. The higher values of K_{ads} . Refer to a higher adsorptive and thus a higher inhibiting effect. Therefore, inhibition efficiency of investigated compounds in 1 M HCl solution is in the order: $1 > 2 > 3 > 4$

Thermodynamic parameters obtained from Gibbs-Helmholtz equation according to this equation : [22]

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \tag{7}$$

Plots of ΔG°_{ads} vs. T for adsorption of the used compounds on the surface of C- steel in 1 M hydrochloric acid over the temperature range from 30°C to 50°C are shown in (Fig. 3). The data gave straight lines of intercept ΔH°_{ads} and slope ΔS°_{ads} . From this Figure the order of decreasing inhibition efficiency of the used compounds is as follows: $1 > 2 > 3 > 4$

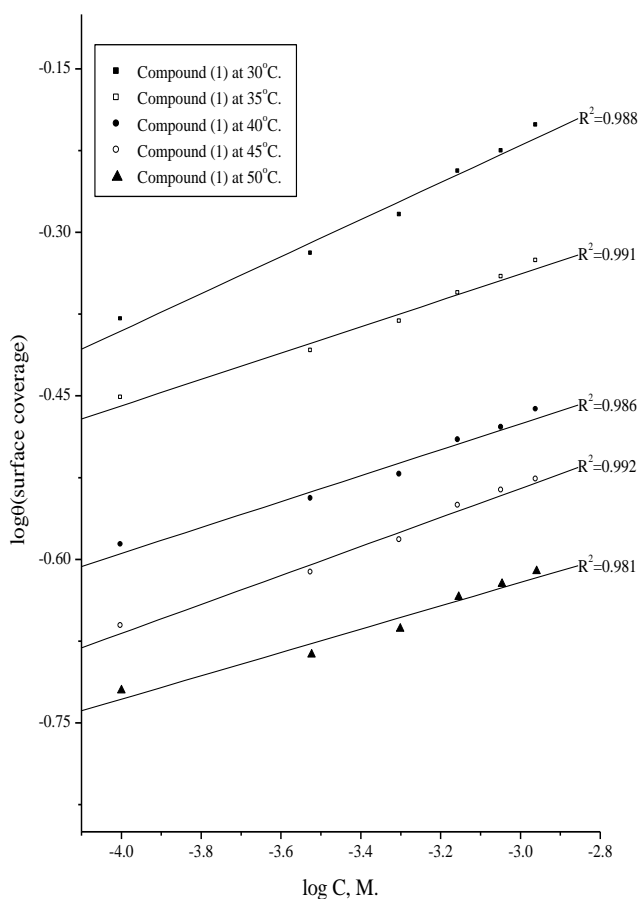


Figure 2. Curve fitting of corrosion data for C – steel in 1 M HCl in presence of different concentrations of inhibitor (1) to Freundlich adsorption isotherm at 30°C , 35°C , 40°C , 45°C , 50°C .

Also the standard adsorption entropy $\Delta S^\circ_{\text{ads}}$ can be obtained, actually calculated on the basis of the from equation (3.7):

$$-\Delta S^\circ_{\text{ads}} = (\partial \Delta G^\circ_{\text{ads}} / \partial T)_p \tag{8}$$

The value of $\Delta H^\circ_{\text{ads}}$ & $\Delta S^\circ_{\text{ads}}$ were calculated and are listed in Table (7). The negative values of $\Delta H^\circ_{\text{ads}}$ and $\Delta S^\circ_{\text{ads}}$ obtained here indicate that the adsorption process is exothermic with an ordered phenomenon. Similar report has been documented [23].

Table 6. Equilibrium constant and adsorption free energy and constant n of the inhibitors adsorbed on C- steel surface.

Inhibitors	Temperature, °C	$-\Delta G^\circ_{\text{ads}}$ kJ.mol ⁻¹	$K_{\text{ads}} \times 10^{-2}$	n
(1)	30	11.8	191	0.17
	35	10.9	129	0.13
	40	10.2	92	0.12
	45	9.6	69	0.12
	50	9.0	51	0.11
(2)	30	11.5	171	0.17
	35	10.7	115	0.15
	40	10.0	83	0.14
	45	9.4	62	0.13
	50	8.8	47	0.12
(3)	30	11.2	156	0.20
	35	10.4	103	0.18
	40	9.7	75	0.17
	45	9.1	57	0.17
	50	8.5	43	0.11
(4)	30	11.0	142	0.20
	35	10.2	95	0.18
	40	9.5	69	0.18
	45	8.9	52	0.17
	50	8.3	39	0.11

Table 7. The thermodynamic parameters for adsorption of the inhibitors on the surface of C- steel in 1 M HCl.

Inhibitors	$-\Delta H^\circ_{\text{ads}}$ kJ mol ⁻¹	$-\Delta S^\circ_{\text{ads}}$ J mol ⁻¹ K ⁻¹
(1)	52.9	140
(2)	51.9	130
(3)	51.6	130
(4)	51.5	120

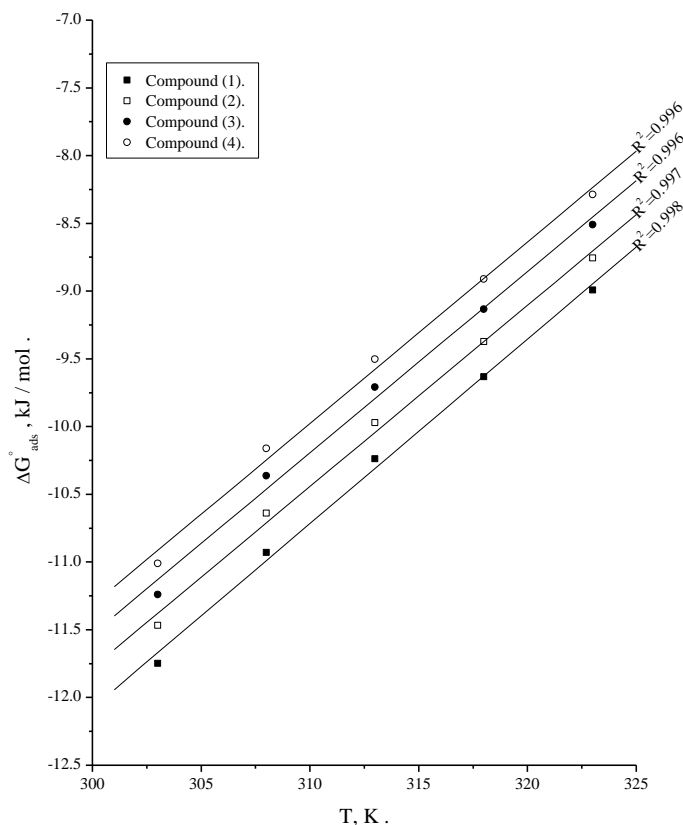


Figure 3. The free energy of a adsorption ΔG_{ads}° for corrosion of C – steel in 1 M HCl in presence of the inhibitors investigated at different temperatures.

3.1.3. Effect of temperature and activation parameters of inhibition process

The effect of temperature on the corrosion rate of C- steel in 1 M HCl over the temperature range (30 to 50 °C) in the absence and presence of different concentrations of the investigated compounds has been studied. The % inhibition efficiency is found to decrease with increasing the temperature; this indicated that, these compounds are physically adsorbed on the C- steel surfaces.

Plots of logarithm of corrosion rate (log k), with reciprocal of absolute temperature (1/T) for C- steel in 1 M HCl at 11×10^{-4} M after 120 min. for the used compounds are shown in (Fig. 4). As shown from this Figure, straight lines with slope of $-E_a^* / 2.303R$ and intercept of A were obtained according to Arrhenius-type equation:

$$k = A \exp (- E_a^* / RT) \tag{9}$$

where: k is the corrosion rate, A is a constant depends on a metal type and electrolyte, E_a^* is the apparent activation energy, R is the universal gas constant and T is the absolute temperature.

Plots of log (corrosion rate/ T) vs. 1/ T for C- steel in 1 M HCl at 11×10^{-4} M after 120min. for the used compounds are shown in (Fig. 5). As shown from this Figure, straight lines with slope of (-

$\Delta H^*/ 2.303R$) and intercept of $(\log R/ Nh + \Delta S^*/ 2.303R)$ were obtained according to transition state equation:

$$\text{Rate} = RT/ Nh \exp (\Delta S^*/ R) \exp (-\Delta H^*/ RT) \tag{10}$$

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

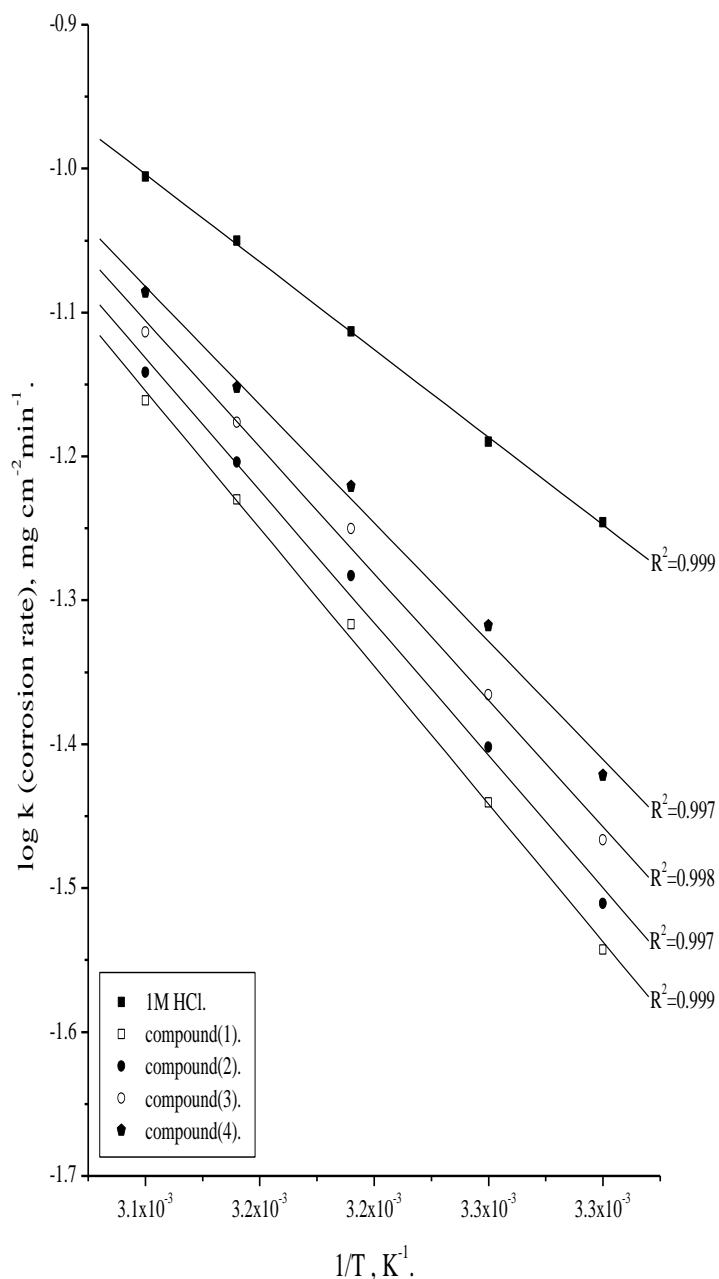


Figure 4. log corrosion rate 1/T curves for the corrosion of C – steel in 1 M HCl at 11x10⁻⁴ M after 120 min. for the inhibitors.

Table 8. Activation parameters of the corrosion of C- steel in 1 M HCl at 11×10^{-4} M after 120 min. immersion for the inhibitors.

Inhibitors	Activation parameters		
	E_a^* , kJ mol ⁻¹	ΔH^* , kJ mol ⁻¹	$-\Delta S^*$, J mol ⁻¹ K ⁻¹
Free acid	23.3	20.7	149.5
(1)	36.7	34.1	162.0
(2)	35.3	32.7	165.9
(3)	33.7	31.1	170.3
(4)	31.5	28.9	176.7

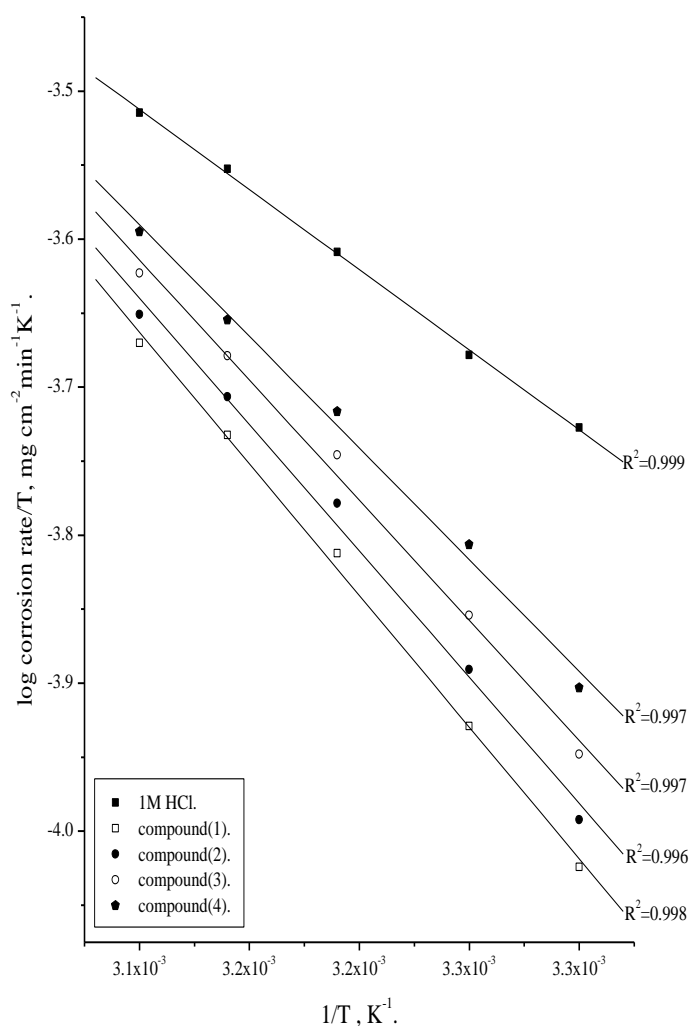


Figure 5. log (corrosion rate/T) – (1/T) curves for the corrosion of C – steel in 1 M HCl at 11×10^{-4} M after 120 min. for the inhibitors.

The calculated values of the apparent activation energy, E_a^* , activation enthalpies, ΔH^* and activation entropies, ΔS^* are given in Table (8). The increase in the activation energy in the presence of

inhibitors indicates the higher inhibition efficiency of the inhibitors. Also the E_a^* values are ranged between 31.5 and 36.7 kJ mol⁻¹ which is attributed to the physisorption of inhibitors on the metal surface [24-26]. This suggests a similar inhibition mechanism for the inhibitors. The increase in E_a^* in case of the protected C- steel with the addition of 11x10⁻⁴ M of the different inhibitors indicates that the energy barrier for the corrosion reaction increases. The increase in E_a^* of the corrosion process could be attributed to the adsorption of the inhibitor molecules onto the metal surface which decreases the interaction between the corrosive medium and the metal surface. The entropy of activation (ΔS^*) in the blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step [27-28]. The value of the activation energy for the corrosion of C- steel in 1 M HCl solution in the absence of the additives is equal to 23.3 kJ mol⁻¹, which is in the same order of the magnitude as those observed [3], 21.26 kJ mol⁻¹ for the corrosion of C- steel in hydrochloric acid Solution and 30.2 kJ mol⁻¹ for corrosion of C- steel in 2 M HCl [29]. The order of decreasing inhibition efficiency of the investigated compounds as gathered from the increase in E_a^* and ΔH_{ads}^* values and decrease in ΔS_{ads}^* values, is as follows: 1 > 2 > 3 > 4

3.2. Potentiodynamic polarization measurements

(Fig. 6) shows the potentiodynamic polarization curves for C- steel dissolution in 1 M HCl in the absence and presence of different concentrations of inhibitor (1) that the most effective one at 30 °C. Similar curves were obtained for other inhibitors (not shown).

The numerical values of the variation of corrosion current density (j_{corr}), corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), degree of surface coverage (θ) and inhibition efficiency (% IE) with the concentrations of the investigated compounds are given in table (9). The results indicated that:

1- The cathodic and anodic curves obtained exhibit Tafel-type behavior. Addition of these compounds increased both cathodic and anodic overvoltages and caused mainly parallel displacement to the more negative and positive values, respectively relative to the blank curve. Thus, the compounds influence both cathodic and anodic process and inhibit both hydrogen evolution and anodic C- steel dissolution. In such cases where the corrosion inhibitor has a greater effect on the cathodic than anodic polarization considerable adsorption of the inhibitor molecule is suggested [30].

2- The data suggested that these compounds act as mixed type inhibitors because there was no definite trend observed in E_{corr} values in the presence of all investigated compounds. In the present study, shift in E_{corr} values is in the range of 40 mV suggesting that they all act as mixed type inhibitors

3- The corrosion potential (E_{corr}) values shifted to less negative values by increasing the concentration of these compounds.

4- The decrease in (I_{corr}) and the increase in inhibition efficiency (% IE) with increasing the additive concentrations are proved that the tested compounds act as corrosion inhibitors for C- steel in 1 M HCl. The higher the values of (β_c) over those of (β_a) suggests that the cathodic reaction is the predominate factor and that the additives act mainly as cathodic inhibitors of the blocking type

5- The order of decreasing inhibition efficiency of the investigated compounds is as follow: 1 > 2 > 3 > 4

This is also in agreement with the observed order of corrosion inhibition by the weight loss method.

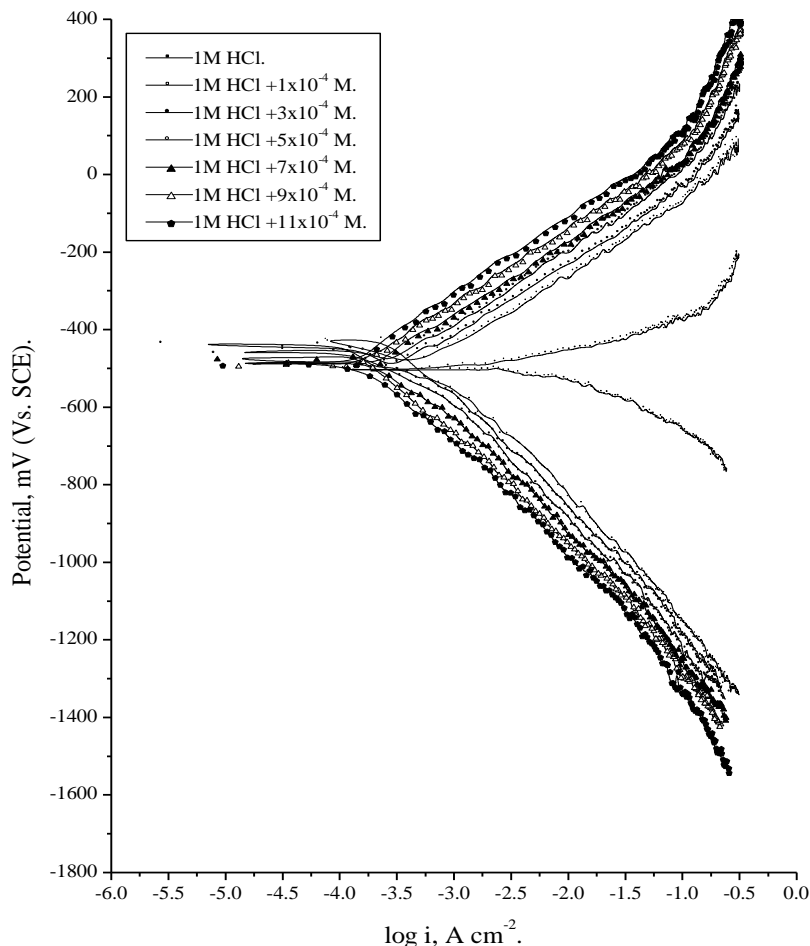


Figure 6. Potentiodynamic polarization curves for the corrosion of C – steel in 1 M HCl in the absence and presence of different concentration of compound (1) at 30 °C

3.3. Electrochemical impedance spectroscopy (EIS)

(Figs. 7) show the Nyquist plots for C- steel in 1 M HCl solution in the absence and presence of different concentrations of the inhibitors(1) similar curves were obtained for other compounds not shown at 30 ±1 °C. The obtained Nyquist impedance diagrams in most cases does not show perfect semicircle, generally attributed to the frequency dispersion as a result of roughness and inhomogenates of the electrode surface. The data reveal that, each impedance diagram consists of a large capacitive loop with low frequencies dispersion (inductive arc). This inductive arc is generally attributed to anodic adsorbed intermediates controlling the anodic process [31-32].

The main parameters deduced from the analysis of Nyquist diagram are:

- The resistance of charge transfer R_{ct} (diameter of high frequency loop)
- The capacity of double layer C_{dl} which is defined as :

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \tag{11}$$

where, f_{max} is the maximum frequency and $\pi = 3.14$

The surface coverage (θ) and the inhibition efficiency obtained from the impedance measurements are defined by the following relations:

$$\theta = \left(1 - \frac{R_{ct}^o}{R_{ct}}\right) \tag{12}$$

$$\% IE = \left(1 - \frac{R_{ct}^o}{R_{ct}}\right) \times 100 \tag{13}$$

where R_{ct}^o and R_{ct} are the charge transfer resistance in the absence and presence of different concentrations of inhibitor, respectively, and are recorded in Table (10).

Table 9. Electrochemical parameters for C- steel in 1 M HCl in the absence and presence of different concentrations of inhibitors at 30 °C.

Inhibitors	Concentration M	-E _{corr} mV	j _{corr} μA cm ⁻²	-β _c mV dec ⁻¹	β _a mV dec ⁻¹	θ	% IE
(1)	0	524	410	296	155	-----	-----
	1x10 ⁻⁴	502	223	259	197	0.456	45.6
	3x10 ⁻⁴	499	153	248	205	0.628	62.8
	5x10 ⁻⁴	490	105	238	208	0.743	74.3
	7x10 ⁻⁴	488	72	227	218	0.825	82.5
	9x10 ⁻⁴	486	53	225	220	0.871	87.1
	11x10 ⁻⁴	485	42	223	222	0.897	89.7
(2)	1x10 ⁻⁴	524	235	283	181	0.427	42.7
	3x10 ⁻⁴	352	182	260	175	0.557	55.7
	5x10 ⁻⁴	522	110	245	213	0.732	73.2
	7x10 ⁻⁴	521	81	241	222	0.803	80.3
	9x10 ⁻⁴	520	64	238	228	0.845	84.5
	11x10 ⁻⁴	520	50	235	232	0.879	87.9
(3)	1x10 ⁻⁴	494	267	270	172	0.350	35.0
	3x10 ⁻⁴	491	208	236	177	0.492	49.2
	5x10 ⁻⁴	486	128	227	184	0.688	68.8
	7x10 ⁻⁴	484	96	218	190	0.765	76.5
	9x10 ⁻⁴	481	70	216	202	0.829	82.9
	11x10 ⁻⁴	464	53	211	207	0.870	87.0
(4)	1x10 ⁻⁴	523	293	203	158	0.285	28.5
	3x10 ⁻⁴	522	231	202	161	0.436	43.6
	5x10 ⁻⁴	520	143	200	163	0.652	65.2
	7x10 ⁻⁴	520	124	189	167	0.698	69.8
	9x10 ⁻⁴	518	78	186	175	0.810	81.0
	11x10 ⁻⁴	517	56	184	179	0.863	86.3

The data indicate that increasing charge transfer resistance is associated with a decrease in the double layer capacitance and increase in the percentage inhibition efficiency. The decrease in C_{dl} values could be attributed to the adsorption of the inhibitor molecules at the metal surface. The order of inhibition efficiency obtained from EIS measurements is: $1 > 2 > 3 > 4$

Fig.8 Bode plots for effect of inhibitors on the corrosion of C- - steel in 1 M HCl solution in the absence and presence of different concentrations of the inhibitors(1) similar curves were obtained for other compounds not shown at $30 \pm 1^\circ\text{C}$.

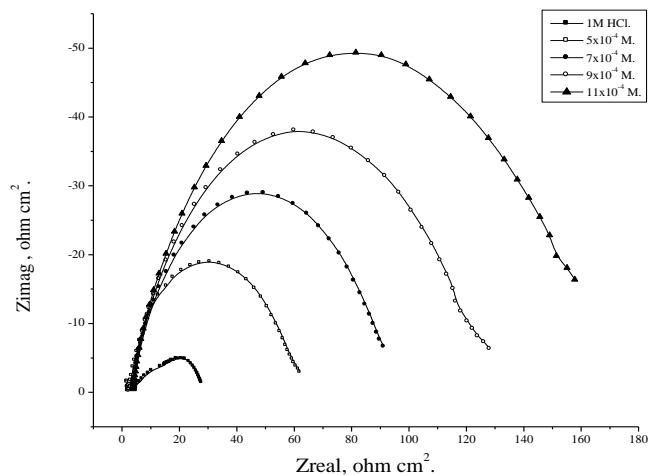


Figure 7. Nyquist plot for the corrosion of C – steel in 1 M HCl in the absence and presence of different concentration of compound (1) at 30°C

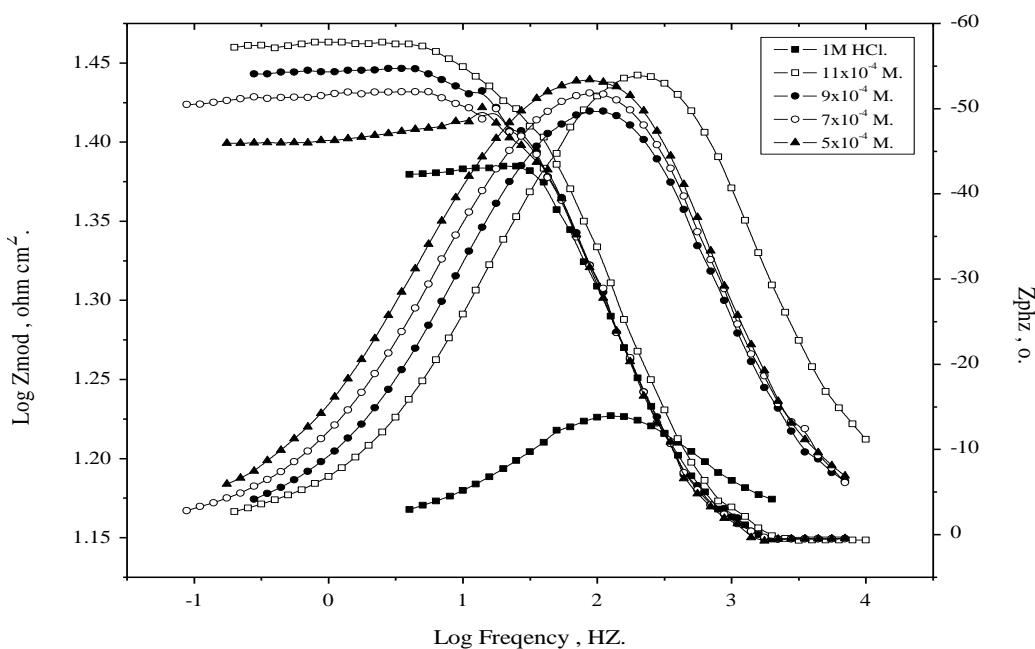


Figure 8. Bode plots for the corrosion of C – steel in 1 M HCl in the absence and presence of different concentration of compound (1) at 30°C

Table 10. Electrochemical kinetic parameters obtained from EIS technique for the corrosion of C-steel in 1 M HCl at different concentrations of inhibitors at 30 °C.

Inhibitors	Concentration M	C_{dl} , $\mu\text{F cm}^{-2}$	R_{ct} , ohm cm^2	θ	% IE
(1)	Blank (1 M HCl)	153.2	11.8	-----	-----
	5×10^{-4}	108.3	46.8	0.748	74.8
	7×10^{-4}	104.7	68.6	0.828	82.8
	9×10^{-4}	98.2	93.4	0.874	87.4
	11×10^{-4}	79.7	112.8	0.895	89.5
(2)	5×10^{-4}	113.2	43.0	0.726	72.6
	7×10^{-4}	101.7	58.3	0.797	79.7
	9×10^{-4}	92.6	83.3	0.858	85.8
	11×10^{-4}	88.2	101.0	0.883	88.3
(3)	5×10^{-4}	114.0	35.1	0.664	66.4
	7×10^{-4}	102.2	53.6	0.780	78.0
	9×10^{-4}	94.8	76.9	0.847	84.7
	11×10^{-4}	93.8	92.2	0.872	87.2
(4)	5×10^{-4}	117.6	34.6	0.658	65.8
	7×10^{-4}	117.5	40.1	0.706	70.6
	9×10^{-4}	111.2	64.6	0.817	81.7
	11×10^{-4}	105.1	89.1	0.867	86.7

3.4. Theoretical calculations of the corrosion inhibition of C- steel by means of organic derivatives in 1 M HCl

The researchers are often encouraged to use theoretical data in their studies not only to support their experimental results and but also to find the efficient way to minimize the chemical expenditures. Therefore, recently more corrosion publications contain substantial quantum chemical calculations [Gece., (2008)]. PM3 liquid phase method was used in the calculations since it has proved to be highly reliable for calculating the physical properties of molecules [33]. The optimized structures of investigated compounds (1-4) with minimum energies obtained from the calculations are given in Fig. (9).

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between frontier orbital's (HOMO and LUMO) of reacting species [34]. Thus, the treatment of the frontier molecular orbital's separately from the other orbital's is based on the general principles governing the nature of chemical reactions.

Fig. (9) represents HOMO views of optimized investigated compounds (1-4) is often associated with the electron donating ability of a molecule. Several researches have shown that the adsorption of an inhibitor on the metal surface can occur on the basis of donor-acceptor interactions between the p-electrons of the investigated compounds and the vacant d-orbital of the metal surface atoms [35-36]. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital.

Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer.

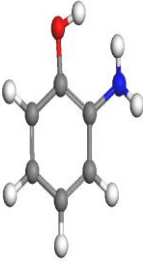
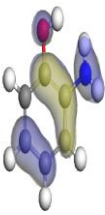
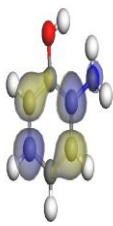
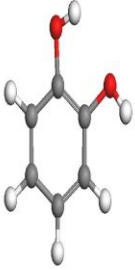
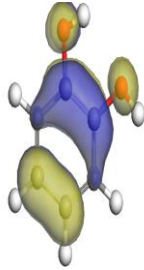
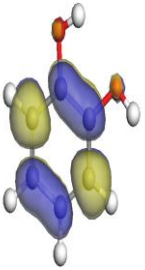
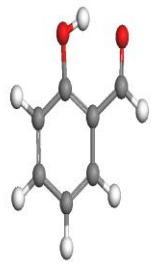
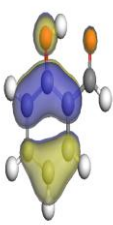
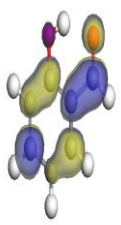
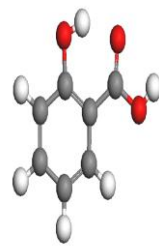
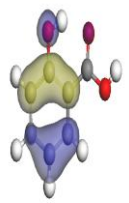
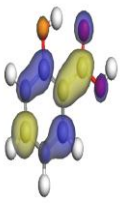
Inhibitors	Optimized Structure	HOMO Views	LUMO Views
(1)			
(2)			
(3)			
(4)			

Figure 9. Optimized, HOMO & LUMO structures of investigated compounds (1-4).

Fig. (9) represents LUMO views of optimized investigated compounds (1-4). E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of E_{LUMO} , the more probable it is that the molecule would accept electrons. The dipole moment (μ) is another indicator of the electronic distribution in a molecule and is one of the properties used to discuss and to rationalize the structure [37], the comparison between the calculated dipole moments of the investigated compounds reveals that the lowest (i.e. compound 1) has better inhibition efficiency.

It is further evident that the inhibition efficiency increases with the decrease of ionization of the molecule, which means that the molecule acts as an electron donor when blocking the corrosion reaction. The results of Table (11) were calculated at 5×10^{-4} M containing quantum parameters $i_{corr.}$, $\log i_{corr.}$, E_{HOMO} , E_{LUMO} , gap difference ($\Delta = E_{LUMO} - E_{HOMO}$), dipole moment (μ) (Debye) and % inhibition efficiency and show that the energies of HOMO orbital of the additives decrease in the following order: $1 > 2 > 3 > 4$

Table 11. Quantum chemical parameters of organic additives.

Inhibitors	$i_{corr.}$ $\mu A cm^{-2}$	$\log i_{corr.}$ $\mu A cm^{-2}$	$-E_{HOMO}$ eV	$-E_{LUMO}$ eV	ΔE eV	μ Debye	% IE
(1)	105	2.02	8.964	0.028	8.936	2.620	74.3
(2)	110	2.04	9.240	0.299	8.941	2.929	73.2
(3)	128	2.11	9.534	0.725	8.809	4.384	68.8
(4)	143	2.16	9.625	0.807	8.818	3.675	65.2

3.5. Chemical structure of the inhibitors and its effect on the corrosion inhibition.

Inhibition of corrosion of C- steel in 1 M HCl by the investigated compounds as measured by chemical and electrochemical techniques were found to depend on both the concentration and the nature of the inhibitor. The observed corrosion data in presence of the inhibitors namely:

- 1- The decrease of corrosion rate with increasing the concentration of the inhibitor.
- 2- The linear variation of weight loss with time.
- 3- The decrease in corrosion inhibition with increasing temperature.
- 4- The parallel shift in Tafel lines to higher potential values.

These observations indicate that the corrosion inhibition is due to adsorption of the inhibitors at the electrode-solution interface. However, inhibition efficiency of the additive compounds depends on many factors [38], which include the number of adsorption active centers in the molecule, and their charge density, complex formation molecular size, and mode of interaction with metal surface. It is generally believed that the adsorption of the inhibitor at the metal/ solution interface is the first step in the mechanism of inhibitor action in aggressive acid media.

The order of decreasing inhibition efficiency of the tested additives is: $1 > 2 > 3 > 4$

This order due to presence of electron donating groups in compounds (1) and (2) but compounds (3) and (4) have electron withdrawing groups, The order of inhibition efficiency of

investigated compounds, as given by weight loss and electrochemical techniques decreases in the following order: $-\text{NH}_2 > -\text{OH} > -\text{CHO} > -\text{COOH}$

It is obvious from above sequence that, compounds containing electron donating groups are more efficient than compounds containing electron withdrawing groups. The electron donating groups enhance adsorption and increase the surface area covered by the compound also electron donating groups with lone pairs on the atoms adjacent to the π system activate the aromatic ring by increasing the electron density on the ring through a resonance donating effect. The resonance only allows electron density to be positioned at the ortho- and para- positions. Hence these sites are more nucleophilic, and the system tends to react with electrophiles at these ortho- and para- sites. Strongly activating electron donating groups add electron density to the p system making it more nucleophilic and consequently, increase the inhibition efficiency.

Compound (1) containing $-\text{NH}_2$ group is more basic and more efficient than $-\text{OH}$ group in compound (2) due to reactivity towards electrophilic substitution reaction and facilitate the formation of stable complex, because it increases the electron density at the ring. So compound (1) which contain N- atom ($-\text{NH}_2$) which is more donating atom than O- atom ($-\text{OH}$) in compound (2) and hence facilitate the formation of complexes with the metal surface.

Compound (3)&(4) are less in the inhibition efficiency because they are electron withdrawing groups. with π bonds to electronegative atoms adjacent to the π system which deactivate the aromatic ring by decreasing the electron density on the ring through a resonance withdrawing effect. The resonance only decreases the electron density at the ortho- and para- positions. Hence these sites are less nucleophilic, and so the system tends to react with electrophiles at the meta sites. Moderately deactivating electron withdrawing groups remove electron density from the p system making it less nucleophilic. Resonance effects are those that occur through the π system and can be represented by resonance structures. Compound (3) is more efficient than compound (4), because $-\text{CHO}$ group is less electron withdrawing than $-\text{COOH}$ group. So, the order of inhibition efficiency is as follows: $1 > 2 > 3 > 4$

4. CONCLUSIONS

1. The investigated compounds are efficient inhibitors for C- steel dissolution in 1 M HCl.
2. The adsorption of these compounds on the C- steel surface was found to obey freundlich adsorption isotherm and thermodynamic parameters are calculated.
3. From the effect of temperature, the activation parameters for the corrosion process (E_a^* , ΔH^* and ΔS^*) were calculated.
4. Percentage inhibition (% IE) increased in the presence of 1×10^{-2} M KI, KSCN and KBr due to the synergistic effect.
5. Potentiodynamic polarization data indicated that these compounds influence both cathodic and anodic processes.

6. The order of the inhibition efficiency of the inhibitors as given by polarization measurements and EIS measurements is in good agreement with that obtained from weight loss measurements. This order was explained on the basis of the chemical structure and adsorption active centers of the compounds.

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