

Synergistic Effect of Potassium Iodide with Some Heterocyclic Compounds on the Corrosion Inhibition of 304 Stainless Steel in Hydrochloric Acid Solution

Abd El-Aziz S. Fouda¹ · Ali M. El-Azaly²

Received: 13 June 2017 / Revised: 8 September 2017 / Accepted: 14 September 2017 / Published online: 4 October 2017
© Springer International Publishing AG 2017

Abstract The inhibitive effect of some heterocyclic organic compounds on the corrosion of 304 stainless steel (304 SS) in 1 M HCl was studied using weight loss, open potential circuit, potentiodynamic polarization and electrochemical impedance spectroscopy techniques at room temperature. The polarization curves revealed that these investigated compounds act as mixed-type inhibitors. Adsorption of these inhibitors on 304 SS surface was found to obey the Langmuir adsorption isotherm. Results showed that the corrosion rate of SS increased with raising temperature and decreased in the presence of investigated compounds. The highest inhibition efficiency of 70.1% was observed with these investigated compounds. An improved inhibition efficiency of 94.5% was observed with the mixture of these compounds and KI at 25 °C in 1 M HCl. This indicates that these compounds were assumed to adsorb on SS surface via physical adsorption. The reactivity of these compounds was analyzed through theoretical calculations based on semi-empirical theory

Keywords Corrosion inhibition · 304 SS · HCl · Heterocyclic compounds · Synergistic effect

1 Introduction

Stainless steels, due to its high strength, workability and high corrosion resistance, are used in various scientific and engineering applications like chemical and pharmaceutical industry [1, 2], food and beverage industry [3], petrochemical industry [4–6], oil and water pipe lines [7], ship and naval structures [8, 9], architectural applications, water supply and desalination plants [10]. However, their weak point is the susceptibility to localized corrosion in the presence of aggressive ions such as chloride ions. HCl is used frequently for acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. The application of acid corrosion inhibitors in the industry is widely used to prevent or minimize material loss during the contact with acid. It has been shown that organic compounds contain heteroatoms with high charge density, such as nitrogen, sulfur and oxygen or those containing multiple bonds, are effective acid corrosion inhibitors [11–21]. The efficiency of the heteroatoms in the decreasing order is as follows: Se < S < N < O. Morpholinium caprylate, morpholinium sebacate and laurate [22, 23], morpholinium oleate [24] and morpholinium stearate [25] have been investigated as inhibitors for steel. Azoles and its derivatives were used as corrosion inhibitors for SS in acid medium [26]. The inhibiting action of these compounds is related to the presence of more than one atom with unshared electron pairs. The relation between the inhibition mechanism and variation in the electronic structure of the inhibitor has been studied [27–29]. The corrosion inhibition of these synthesized organic compounds is mainly because of physical or chemical adsorption resulting from the interaction of polar centers of the inhibitor's molecule with active sites on the metal surface [30, 31]. As a fact, the investigated heterocyclic compounds are the potential inhibitors for their structure containing oxygen and nitrogen atoms.

✉ Abd El-Aziz S. Fouda
asfouda@hotmail.com

Ali M. El-Azaly
dr_alielazaly_81@yahoo.com

¹ Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura 35516, Egypt

² Nile Higher Institute for Engineering and Technology, El-Mansoura, Egypt

These investigated compounds have relatively high molecular size, contain more than one benzene ring, more than one active center, and are synthesized easily from cheap raw material. In order to develop the new effective corrosion inhibitors, the aim of the present work is to investigate the highest inhibition performance of these investigated compounds as suitable inhibitors for control of corrosion of 304 SS in 1 M HCl solution.

2 Experimental

2.1 Materials and Solutions

The experiments were performed with type SS 304 having the following chemical composition (wt %): 0.03 C, 0.04 P, 0.08 C, 0.75 Si, 2 Mn, 8–11 Ni, 18–20 Cr and the rest is iron. 304 SS specimens were abraded with different grades of emery papers, ultrasonically degreased in acetone [32], rinsed in doubly distilled water and finally dried between two filter papers at room temperature. Double distilled water and analytical reagent grade HCl were used for preparing solutions. The molecular structures, names, molecular weights and molecular formulas of the investigated compounds are shown:

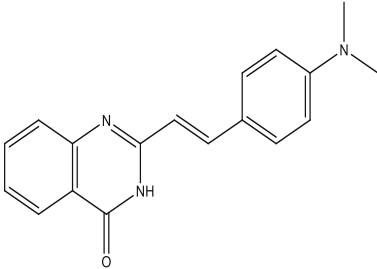
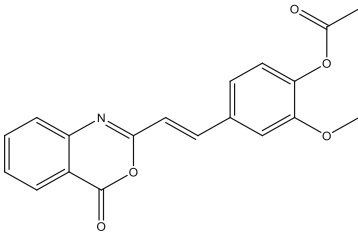
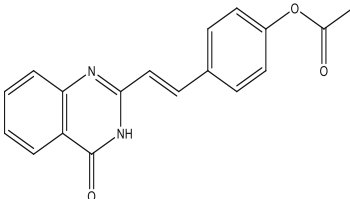
2.2 Methods

2.2.1 Weight Loss (WL) Technique

The reaction container used in this method was a graduated glass vessel 8 cm inner diameter and having a total volume of 150 ml. Hundred milliliters of the test solution was employed in each experiment. The test pieces were cut nearly $20 \times 20 \times 0.2$ mm. The specimens were prepared as before and then weighed. The test pieces were suspended by suitable glass hooks at the edge of the beaker and under the surface of the test solution by about 1 cm. After specified periods of time, the test pieces were taken out from the test solution, rinsed in doubly distilled water, dried and weighed again and the value of WL in mg has been reported. Each reading reported is an average of three experimental readings recorded to the nearest 0.001 g on a mettler AE166 analytical balance.

2.2.2 Electrochemical Techniques

Three electrochemical techniques (PP and EIS) have been employed for studying the corrosion inhibition of 304 SS with and without different doses from investigated compounds. Measurements were taken in a standard glass three-electrode cell with a capacity of 150 ml. The counter

Inh.	Names	Structures	Mol formulas	Mol. weights
A	(<i>E</i>)-2-(4-(dimethylamino)styryl)quinazolin-4(3 <i>H</i>)-one		$C_{18}H_{17}N_3O$	291.35
B	(<i>E</i>)-2-methoxy-4-(2-(4-oxo-4 <i>H</i> -benzo[d][1,3]oxazin-2-yl)vinyl)phenyl acetate		$C_{19}H_{15}NO_5$	337.33
C	(<i>E</i>)-4-(2-(4-oxo-3,4-dihydroquinazolin-2-yl)vinyl)phenyl acetate		$C_{18}H_{14}N_2O_3$	306.32

and the reference electrodes are platinum and saturated calomel (SCE), respectively. 304 SS strips with an exposed area of 1 cm² were used as working electrode. These measurements were taken using Potentiostat/Galvanostat (Gamry PCI 300/4) and a personal computer with EIS 300 software for calculations.

2.2.2.1 Potentiodynamic Polarization (PP) Technique A constant quantity of the test solution (100 ml) was taken in the polarization cell. A time interval of about 1800 s was given for the system to attain a steady state, and the open-circuit potential (OCP) was noted. Current–potential curves were recorded by changing the electrode potential automatically from − 150 to + 150 mV with scanning rate 0.5 mVs^{−1}. Solutions were not deaerated to make the conditions identical to WL measurements. All the experiments were carried out at 25 °C. The procedure adopted for the PP and EIS measurements was the same as described elsewhere [33]. All experiments were repeated at least three times for check their reproducibility.

2.2.2.2 EIS Method The EIS spectra were recorded at open-circuit potential, OCP after immersion of the electrode for 1800 s. The AC signal was 5 mV peak to peak, and the frequency range studied was between 100 kHz and 0.1 Hz. In each measurement in electrochemical techniques, at least three closer results were considered, and their average values have been reported.

3 Results and Discussion

3.1 Corrosion Behavior of 304 SS by WL Method

The corrosion behavior of 304 SS in 1 M HCl in the presence and absence of compound (A) at 25 °C was studied and is represented in Fig. 1. As shown in this figure, by increasing the dose of this compound, the WL of 304 SS samples was decreased. This means that the presence of this compound retards the corrosion of 304 SS in 1 M HCl or in other words, and this derivative (A) acts as inhibitor. The values of % IE of investigated compounds are given in Table 1. From this table, the order of the IE of the investigated compounds is as follows: A > B > C. It is obvious that the IE increases with increasing the doses of the investigated compounds.

3.2 Adsorption Isotherms

The adsorption of an organic compound on the surface of a metal is regarded as a substitutional adsorption processes between the organic compound in aqueous phase, org_(aq),

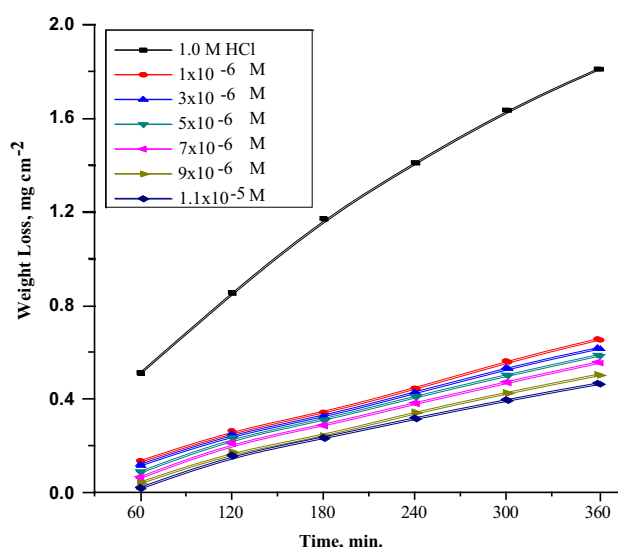
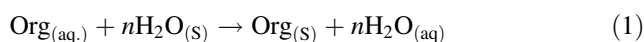


Fig. 1 WL–time curves for the corrosion of 304 SS in 1 M HCl with and without different doses of inhibitor (A) at 25 °C

Table 1 % IE of the investigated compounds at different doses as determined from WL method at 25 °C; duration of immersion is 240 min

(Inhibitor) (× 10 ⁶ M)	% IE		
	A	B	C
1	68.4	55.5	43.5
3	69.6	60.4	52.2
5	70.8	63.6	56.4
7	72.8	66.9	60.6
9	75.0	71.2	66.1
11	76.3	74.3	70.8

and the water molecule adsorbed on the electrode surface [34, 35]:



where *n* is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. According to Bockris and Swinkless [36], *n* is assumed to be independent of coverage or charge of electrode. Clearly, the value of *n* depends on the cross-sectional area of organic molecule with respect to that of water molecule. At equilibrium, the chemical potential (*μ*) on both sides is equal. Now depending on the expression of (*θ*), as related to the physical model adopted to describe adsorption of, a number of mathematical relations have been suggested to fit the various experimental data available. The simplest theoretical equation is that due to Langmuir and given by the equation [37]

$$f(\Theta, x) \exp(-a, \Theta) = KC \tag{2}$$

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. All adsorption expressions include the K, which is related to the standard free energy of adsorption (ΔG_{ads}^o) by:

$$K = 1/55.5 [\exp - \Delta G_{ads}^o / RT] \tag{3}$$

where R is the universal gas constant and T is the absolute temperature. Plots of C/Θ versus C (Langmuir's isotherm) for adsorption of the investigated compounds on the surface of 304 SS in 1 M HCl at 25 °C are shown in Fig. 2. The data gave straight lines with slopes nearly unity indicating that Langmuir's isotherm is valid for these systems, and also, the values of R^2 are near to unity. On the other hand, it is found that the kinetic-thermodynamic model of El-Awady et al. [38] is valid to operate the present adsorption data:

$$\text{Log} [\Theta / (1 - \Theta)] = \text{log } K' + y \text{log } C \tag{4}$$

The equilibrium constant of adsorption is $K = K'^{(1/y)}$, where $1/y$ is the number of the surface active sites occupied by one inhibitor molecule and C is the bulk concentration of the inhibitor. By plotting $\text{log} [\Theta / (1 - \Theta)]$ against $\text{log } C$ at 25 °C, a straight line relationships were obtained (Fig. 3) suggesting the validity of this model for all cases studied. The calculated values of $1/y$, K and ΔG_{ads}^o are given in Table 2. Inspection of the data recorded in Table 2 shows that the large values of ΔG_{ads}^o and its negative sign indicate that the adsorption of the investigated compounds on 304 SS surface is proceeding spontaneously and is accompanied by a highly efficient adsorption. It is worth

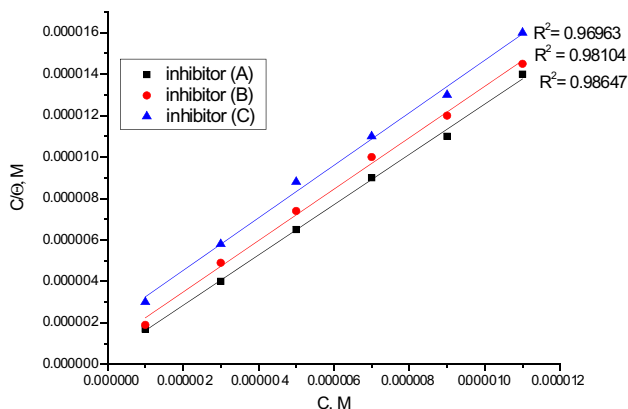


Fig. 2 Langmuir adsorption isotherm plotted for the corrosion of 304 SS in 1 M HCl at 25 °C as obtained from WL method

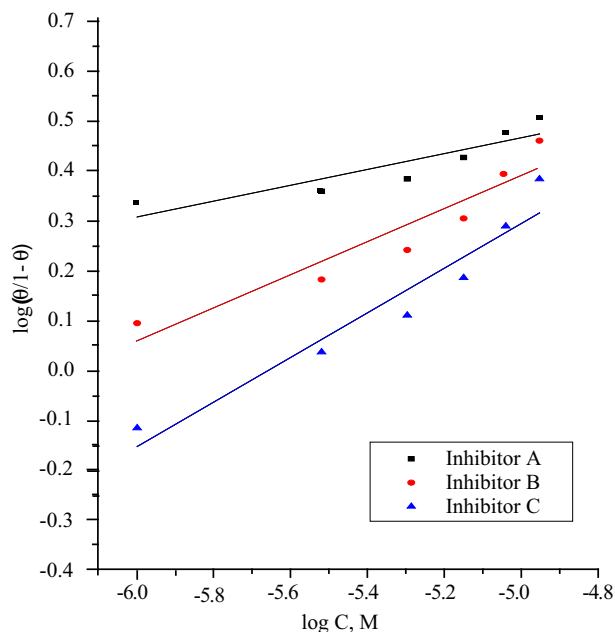


Fig. 3 El-Awady kinetic model plotted for the corrosion of 304 SS in 1 M HCl at 25 °C as obtained from WL method

Table 2 Number of active sites ($1/y$), slopes of Langmuir isotherm lines, equilibrium constants (K), and free energy of adsorption (ΔG_{ads}^o) for all investigated compounds obtained from WL measurements at 25 °C

Inh.	Kinetic model			Langmuir isotherm		
	$1/y$	$K \times 10^5$ M^{-1}	$-\Delta G_{ads}^o$ $kJ mol^{-1}$	Slope	$K \times 10^4$ M^{-1}	$-\Delta G_{ads}^o$ $kJ mol^{-1}$
A	6.3	860.8	55.2	1.1	252	46.5
B	3.0	14.9	45.2	1.1	101	44.2
C	2.2	4.6	42.2	1.1	60	42.9

noting that the value of $1/y$ is more than unity. This means that the given inhibitor molecules will occupy more than one active site. In general, the values of ΔG_{ads}^o obtained from El-Awady et al. model are comparable with those obtained from Langmuir's adsorption isotherm. From these results, it may be generalized that the more efficient inhibitor has more negative ΔG_{ads}^o , so the order of IE is as follows: $A > B > C$.

3.3 The Study of the Corrosion Behavior of SS 304 by PP Method

Polarization curves of 304 SS corrosion in 1 M HCl with and without different doses of compound (A) at 25 °C are illustrated in Fig. 4. The numerical values of the variation

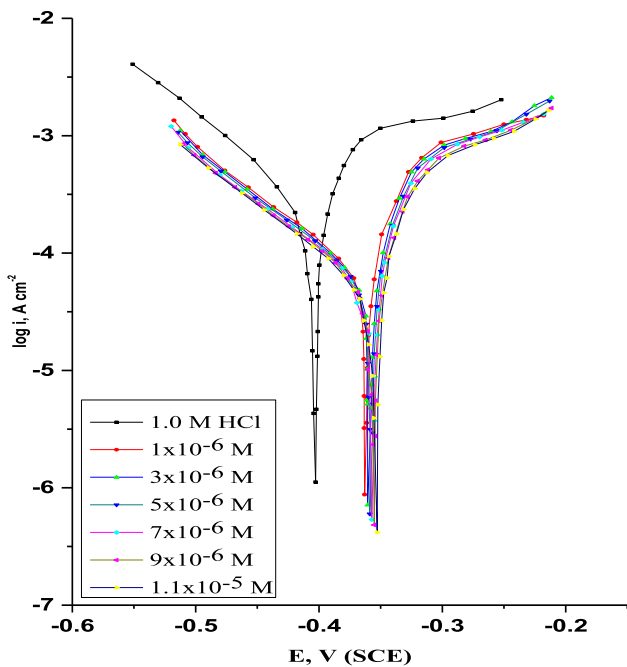


Fig. 4 PP curves of 304 SS in 1 M HCl with and without different doses of compound (A) at 25 °C

of corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), corrosion rate, (θ) and % IE with the doses of compound (A) are given in Table 3. The results of this table indicated that by increasing the dose of the inhibitor, i_{corr} decreases and hence, % IE increases. Table 4 represents the % IE of the investigated compounds as determined from PP technique. The results of this table follow the following order: A > B > C. The results of Table 4 indicate that the presence of inhibitors affects both the anodic metal dissolution and cathodic hydrogen evolution; this indicates that these inhibitors act as mixed-type inhibitors and also E_{corr} values was enhanced with no definite trend.

Table 4 IE at different doses of the investigated compounds as determined from PP method at 25 °C

(Inh.) × 10 ⁶ M	% IE		
	A	B	C
1	70.1	54.5	45.5
3	71.4	59.2	54.1
5	72.7	65.2	58.4
7	74.9	67.3	61.4
9	76.1	70.7	65.3
11	77.0	72.6	68.1

Table 5 % IE at different doses of inhibitors in the presence of 1 × 10⁻² M KI as determined from PP method at 25 °C

(Inhibitor) (× 10 ⁶ M)	% IE		
	A	B	C
1	94.5	92.2	91.2
3	95.0	93.3	92.7
5	95.5	93.9	92.2
7	96.0	94.3	92.0
9	96.4	94.8	91.6
11	96.8	95.9	90.6

3.4 Synergistic Effect

Iodide ion is found to enhance the inhibitive effect of several inhibitors in acid solutions. In the present study, the influence of iodide ion on the inhibitive performance of the investigated compounds has been studied. Similar results have been documented [39]. Table 5 shows the influence of 0.01 M KI on IE of various doses of the investigated compounds for 304 SS using PP technique. It can be seen from this table that the addition of KI increases the IE of

Table 3 Effect of doses of compound (A) on the electrochemical parameters of 304 SS in 1 M HCl at 25 °C

(Inh.) (× 10 ⁶ M)	-E _{corr} mV	i _{corr} μA cm ⁻²	-β _c mV dec ⁻¹	β _a mV dec ⁻¹	CR mm year ⁻¹	θ	% IE
Blank	396	220.4	95	86	2.517	-	-
1	363	66.0	134	70	0.754	0.701	70.1
3	363	63.1	135	70	0.721	0.714	71.4
5	361	60.3	136	70	0.688	0.727	72.7
7	361	55.3	137	71	0.631	0.749	74.9
9	360	52.7	135	71	0.601	0.761	76.1
11	359	50.8	136	71	0.580	0.770	77.0

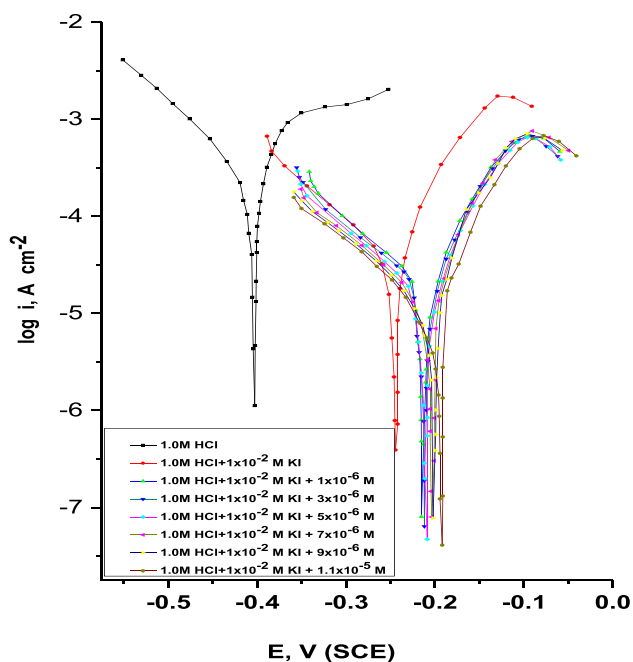


Fig. 5 PP curves of 304 SS in 1 M HCl in the absence and presence of 1×10^{-2} M KI and different doses of compound (A) at 25 °C

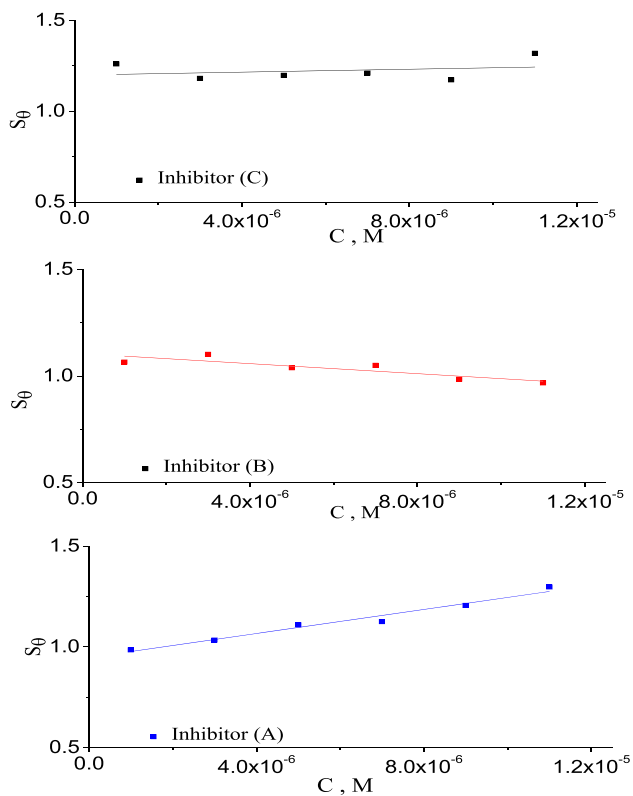


Fig. 6 Plots of synergism parameters S_0 of KI versus the doses of the investigated compounds at 25 °C

Table 6 Inhibition efficiency of 1×10^{-6} M investigated compounds at different temperatures as determined from WL method; duration of immersion is 240 min

Temp. (°C)	(% IE)		
	A	B	C
25	68.4	55.5	43.5
35	59.5	49.6	40.1
45	56.2	47.0	37.3
55	52.6	42.1	29.4

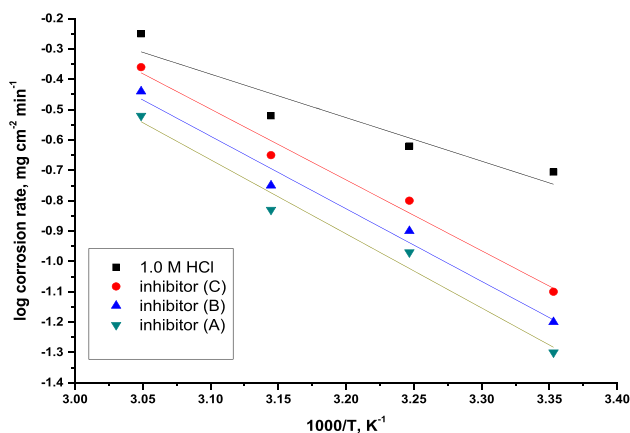


Fig. 7 Plots of log corrosion rate versus $(1000/T)$ for 304 SS dissolution in 1 M HCl in the absence and presence of 1.1×10^{-5} M of investigated compounds

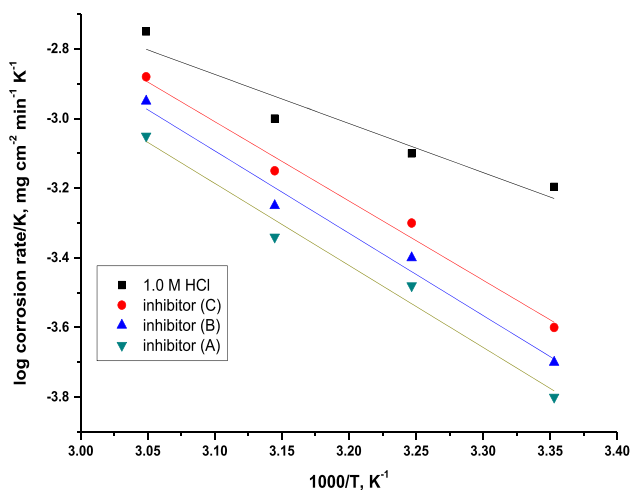


Fig. 8 Plots of log (corrosion rate/ T) versus $(1000/T)$ for 304 SS dissolution in 1 M HCl in the absence and presence of 1.1×10^{-5} M of investigated compounds

the investigated compounds for 304 SS. Figure 5 represents the PP curves of 304 SS in 1 M HCl in the absence and presence of 1×10^{-2} M KI and different doses of inhibitor (A) at 25 °C. The synergistic effect between iodide ions and inhibitor molecules can be explained by the fact that the addition of KI solution stabilizes the adsorption of the investigated compounds on the SS surface. This

Table 7 Thermodynamic activation parameters for the dissolution of 304 SS in 1 M HCl in the absence and presence of 1.1×10^{-5} M of investigated compounds

Inhibitor	E_a^* (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	$-\Delta S^*$ (J mol ⁻¹ K ⁻¹)
Blank	23.6	21.0	187.9
C	45.1	42.5	126.9
B	45.8	43.2	123.2
A	46.1	43.4	121.0

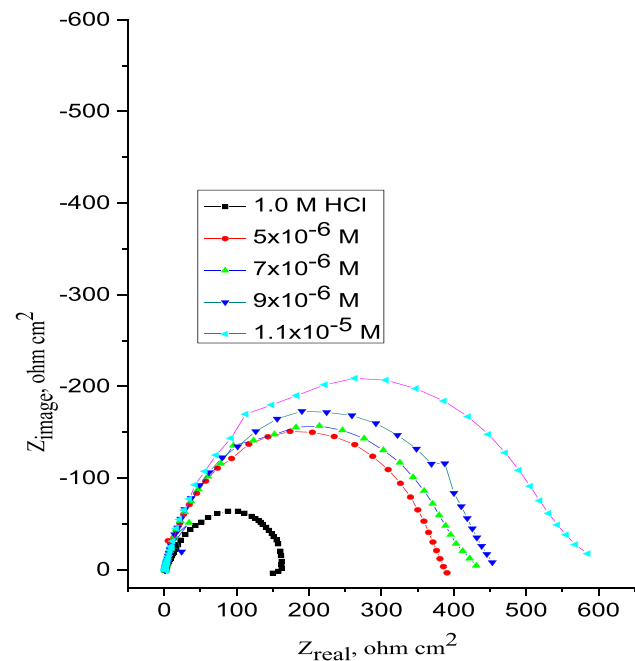


Fig. 9 The Nyquist plots for the corrosion of 304 SS in 1 M HCl with and without different doses of inhibitor (A) at 25 °C

stabilization may be caused by the interaction between inhibitor molecule and iodide ions. Thus, the interaction enhances the IE to a considerable extent due to the increase in the surface coverage in the presence of iodide ions. Figure 6 represents the plots of synergism parameters S_θ of KI versus the doses of the investigated compounds at 25 °C. The values of S_θ are almost > 1 ; this means that there is a synergistic effect between the inhibitor molecules and KI.

Aramaki and Hackerman [40] calculated the synergism parameter S_θ using the following equation:

$$S_\theta = (1 - \theta_{1+2}) / (1 - \theta'_{1+2}) \tag{5}$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$, θ_1 surface coverage by anion; θ_2 surface coverage by cation; θ'_{1+2} measured surface coverage by both anion and cation. S_θ approaches unity when there are no interactions between the inhibitor compounds, while $S_\theta > 1$ points

Table 8 Electrochemical kinetic parameters obtained by EIS method for the dissolution of 304 SS in 1 M HCl with and without different doses of the investigated compounds at 25 °C

Inhibitor	(Inh) $\times 10^6$ (M)	C_{dl} $\mu F cm^{-2}$	-Phase degree	R_{ct} ohm cm^2	R_p
1 M HCl	–	235.3	56.7	150.2	137.8
A	5	162.4	67.6	390.0	325.8
	7	147.1	66.3	430.7	343.9
	9	111.2	66.8	453.1	372.8
	11	108.3	64.9	584.9	459.7
B	5	184.7	66.0	343.1	289.8
	7	159.2	67.3	397.9	333
	9	140.2	67.2	451.8	369.4
	11	119.8	69.5	528.8	422.2
C	5	185.0	68.5	315.5	282.4
	7	179.7	66.2	352.6	296.7
	9	171.2	66.9	370.0	303
	11	122.3	69.7	517.9	420.8

Table 9 % IE of different doses of the investigated compounds for the corrosion of 304 SS in 1 M HCl at 25 °C as obtained from EIS method

(Inh) $\times 10^6$ M	% IE		
	A	B	C
5	61.5	56.2	52.4
7	65.1	62.3	57.4
9	66.9	66.8	59.4
11	74.3	71.6	71.0

to a synergistic effect; in the case of $S_\theta < 1$, the antagonistic interaction prevails.

3.5 Effect of Temperature on the Activation Parameters of Corrosion Process

The effect of temperature on the corrosion rate in the temperature range 25–55 °C in the presence and absence of the investigated compounds was studied. From the results obtained in Table 6, the % IE was decreased by increasing the temperature. This indicates that these derivatives are adsorbed on 304 SS surface physically, also the order of IE decreased as follows: A > B > C. The rate of corrosion increases by raising the temperature, due to desorption of adsorbed molecules and leave the metal surface to face the corrosive solution. Figure 7 represents plots of the log rate versus $1/T$, and Fig. 8 shows the relation between log (rate/ T) versus $1/T$ data. The calculated values of the apparent

activation energy, E_a^* , activation entropies, ΔS^* , and activation enthalpies, ΔH^* , are given in Table 7. Generally, one can say that the nature and the dose of electrolyte affect greatly the activation energy of the corrosion process. The results which are presented in Table 7 showed that the ΔH^* of all compounds is positive. The positive sign of the enthalpy reflects the endothermic nature of the SS dissolution process [41]. Also, all the entropies of activation were negative. The negative values of entropies imply that the activated complex in the rate-determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place ongoing from reactants to the activated complex [42].

3.6 EIS Method

The corrosion behavior of 304 SS in 1 M HCl solution in the absence and presence of different doses of the investigated compounds was examined by the EIS technique at 25 °C. Figure 9 shows the Nyquist plots for 304 SS in 1 M HCl solution in the absence and presence of different doses of compound (A). 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:

$$C_{dl} = 1/2\pi f_{max} R_{ct} \quad (6)$$

The θ and the IE obtained from the EIS measurements are defined by the following relation:

$$\%IE = \theta \times 100 = [1 - (R_{ct}^o/R_{ct})] \times 100 \quad (7)$$

where R_{ct}^o and R_{ct} are the charge transfer resistance in the absence and presence of different doses of inhibitor, respectively. The data associated with the impedance diagrams are given in Table 8. Table 9 shows the IE of different doses of the investigated compounds for the corrosion of 304 SS in 1 M HCl at 25 °C as obtained from EIS. From the impedance data given in Tables 8 and 9, one concludes that: (a) the value of R_{ct} increases with the increasing the doses of the inhibitors and hence the increase in the IE in acidic solution, (b) as the impedance diagram obtained has a semicircle appearance, it shows that the corrosion of 304 SS is mainly controlled by a charge transfer process, (c) the value of double-layer capacitance decreases by increasing the inhibitor concentration; this is due to the adsorption of these compounds on the electrode surface leading to a film formation on the 304 SS surface, (d) the % IE obtained from EIS measurements is nearly close to those obtained from PP and WL methods. The order of IE obtained from EIS measurements is: $A > B > C$.

3.7 Chemical Structure of the Investigated Compounds and Corrosion Inhibition

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. Four types of adsorption may take place during inhibition involving organic molecules at the metal/solution interface: (a) electrostatic attraction between charged molecules and charged metal, (b) interaction of unshared electrons pairs in the molecule with the metal, (c) interaction of π electrons with the metal and (d) a combination of the above [43]. Concerning inhibitors, the IE depends on several factors: such as (1) the number of adsorption sites and their charge density, (2) molecular size, heat of hydrogenation, (3) mode of interaction with the metal surface and (4) the formation metallic complexes [44]. Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulfur or oxygen, each of them in principle representing a chemisorption center. The inhibitive properties of such compounds depend on the electron densities surrounding the chemisorptions center: the higher the electron density at the center, the more the effective the inhibitor. The order of the IE of the investigated compounds is: $A > B > C$. The surface coordination is through the oxygen and the nitrogen atoms attached to the hetero ring, and these compounds can be adsorbed in a flat orientation through a bidentate form. It was concluded that the mode of adsorption depends on the affinity of the metal toward the π -electron clouds of the ring system [45]. This behavior can be rationalized on the basis of the structure–corrosion inhibition relationship of organic compounds. Linear free energy relationships (LFER) has previously been used to correlate the IE of organic compounds with their Hammett constituent constants [46]. The LFER or Hammett relation is given by [47, 48]

$$\log R \text{ (rate of corrosion)} \quad \text{or} \quad \log IE = -\rho \sigma \quad (8)$$

where ρ is the reaction constant and σ (Hammett constant) is a relative measure of the electron density at the reaction center. Those constituents which attract electrons from the reaction center are assigned positive σ values, and those which are electron donating have negative σ values. The slope of the plot of $\log R$ or % IE versus σ is ρ , and its sign indicates whether the process is inhibited by an increase or decrease in the electron density at the reaction center. The magnitude of ρ indicates the relative sensitivity of the inhibition process to electronic effects.

Compound (A) contains dimethyl amine group in the para position ($\sigma_p = -0.205$). This group acts as electron-donating group which increases the electron density of the ring and increases the ability of the inhibitor to be adsorbed on the metal surface. Also this compound contains two

nitrogen atoms in the hetero ring. So, compound (A) is the highest effective one. Compound (B) comes after compound (A) in IE because it contains an acetyl group ($-\text{COOCH}_3$) in the para position ($\sigma_p = + 0.39$) which is electron-withdrawing group; on the other hand, this molecule contains a methoxy group in the meta-position which may add electrons to the molecule. Also compound (B) contains N and O atoms in the hetero ring ($\text{N} > \text{O}$ in basicity). All of the above will decrease the electron density on the molecule and hence decrease the adsorption power on the metal surface. Compound (C) is the least effective one due to the presence of acetyl group in the para position in the molecule ($\sigma_p = + 0.39$) which is electron-withdrawing group and contains two nitrogen hetero atoms. On the other hand, compound (B) has larger molecular size than compound (C).

4 Conclusions

The investigated compounds were found to be inhibitors for 304 SS corrosion in HCl solution. The IE decreases with increasing temperature at all temperatures studied (25–55 °C). The inhibition is probably due to the adsorption of these compounds on the metal surface and blocking its active sites by the phenomenon of physical adsorption. The data obtained from this study fit well into the Langmuir's adsorption isotherm and also obey the thermodynamic-kinetic model. Synergistic effect occurs on the addition of KI to acid containing the investigated compounds which inhibits SS corrosion. The phenomenon of synergism takes place at very low doses for the systems studied. Polarization curves proved that the three investigated compounds were mixed-type inhibitors, which can suppress the anodic and cathodic reactions at the same time. EIS plots indicated that these compounds were adsorbed on the electrode surface to form a compact film to inhibit the corrosion process.

References

- Ashassi-Sorkhabi H, Eshaghi M (2009) Corrosion inhibition of mild steel in acidic media by [BMIm] Br Ionic liquid. *Mater Chem Phys* 111:267–271
- Dreyman EW (1998) Corrosion: fundamentals, testing, and protection. *ASM Handb Corros* 13:1221
- Zhang QB, Hua YX (2009) Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. *Electrochim Acta* 54:1881–1887
- Feng Y, Siow KS, Teo WK, Hsieh AK (1999) the synergistic effects of propargyl alcohol and potassium iodide on the inhibition of mild steel in 0.5 M sulfuric acid solution. *Corros Sci* 41:829–852
- Romero JM, Chavez CA, Martinez L, Amaaya M (2002) Localised biological corrosion of X52 steel exposed within sea water pipelines. *Br Corros J* 37:117–121
- Sedriks AJ, Dudts P (2001) Corrosion resistance, coating, and magnetic property issues of nonmagnetic austenitic stainless steels for ship hulls. *Corrosion* 57:84–91
- Sathiyaraj AR, Muralidaran S, Velmurugan S, Venkatachari G (2008) Corrosion inhibitor for the chemical decontamination of primary coolant systems of nuclear power plants. *Mater Chem Phys* 110:269–275
- Athar M, Ali H, Quraishi MA (2002) Corrosion inhibition of carbon steel in hydrochloric acid by organic compounds containing heteroatoms. *Br Corros J* 37:155–158
- Vurinen E, Ngobeni P, Van Der Klashorst GH, Skinner W, De Wet E, Ernst WS (1994) Derivatives of cyclohexylamine and morpholine as volatile corrosion inhibitors. *Br Corros J* 29(2):120–121
- Skinner W, Du Preez F, Vuorinen E (1999) Evaluation of vapour phase corrosion inhibitors. *Br Corros J* 55(2):151–156
- Rodrigues PRP, Aoki IV, DeAndrade AHP, De Oliveria E, Agostinho SML (1996) Effect of benzotriazole on the electrochemical and corrosion behaviour of type 304 stainless steel in 2 M sulphuric acid solution. *Br Corros J* 31(4):305–308
- Kumar A, Borthakur SP, Dhawan HC (1999) Inhibitive action of some mercaptotriazoles towards the corrosion of Fe–Cr–Ni steel in sulphuric acid. *Bull Electrochem* 15(2):63–66
- Cheng XL, Ma HY, Chen SH, Yin R, Chen X, Yao ZM (1999) Corrosion of stainless steels in acid solutions with organic sulfur-containing compounds. *Corros Sci* 41:321–333
- Agrawal R, Nambodhiri TKG (1992) the inhibition of corrosion and hydrogen embrittlement of AISI 410 stainless steel. *J Appl Electrochem* 22:383–389
- Abdallah M (2002) Rhodanine azosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution. *Corros Sci* 44(4):717–728
- Rozenfeld IL (1981) Corrosion inhibitors. Mc-Graw Hill, New York
- Jiang Z, Wang J, Hu Q, Huang S (1995) the influence of 1-(2-pyridylazo)-2-naphthol (PAN) on the corrosion of titanium in 10 N sulfuric acid solution. *Corros Sci* 37:1245–1252
- Ajmal M, Mideen AS, Quraishi MA (1994) 2-Hydrazino-6-methyl-benzothiazole as an effective inhibitor for the corrosion of mild steel in acidic solutions. *Corros Sci* 36:79–84
- Raicheva SN, Aleksiev B, Sokolova EI (1993) the effect of the chemical structure of some nitrogen- and sulphur-containing organic compounds on their corrosion inhibiting action. *Corros Sci* 34:343–350
- Stupnisek-Lisac E, Ademovic Z (1995) In: 8th European symp. corrosion inhibitors, Ferrara, p 257–265
- Quraishi MA (1995) In: 8th European symp. corrosion inhibitors, Ferrara, p 277
- Mahdavian M, Attar MM (2009) electrochemical behaviour of some transition metal acetylacetonate complexes as corrosion inhibitors for mild steel. *Corros Sci* 51:409–414
- Tarlok S, Sharma R, Bawa G, Khanna S (2009) Bonding and structure trends of thiosemicarbazone derivatives of metals—an overview. *Coord Chem Rev* 253:977–1055
- Sastri VS, Perumareddi JR (1997) Molecular orbital theoretical studies of some organic corrosion inhibitors. *Corrosion* 53:617–622
- Lukovits I, Kalman E, Zucchi F (2001) Corrosion inhibitors—correlation between electronic structure and efficiency. *Corrosion* 57:3–8
- Al-Mayouf AM, Al-Amery AK, Al-Suhaybi AA (2001) Comparison of inhibition efficiency of some azoles on corrosion of

- type 304 stainless steel in acidic solutions. *Br Corros J* 36:127–132
27. Bentiss F, Traisnel M, Choibi N, Mernavi B, Vezin H, Lagrenee M (2002) 2,5-Bis (*n*-methoxyphenyl)-1,3,4-oxadiazoles used as corrosion inhibitors in acidic media: correlation between inhibition efficiency and chemical structure. *Corros Sci* 44:2271–2289
 28. Thomas JGN (1980) In: Proceedings of the 5th European symposium on corrosion inhibitors, vol V, suppl. no. 8. Ann University, Ferrara, p 453
 29. Gad Allah AM, Hefny MM, Salih SA, El-Basiouny MS (1989) Corrosion inhibition of zinc in HCl solution by several pyrazole derivatives. *Corrosion* 45(7):475–478
 30. Ostapenko GI, Gloukhov PA, Bunev AS (2014) Document investigation of 2-cyclohexenylcyclohexanone as steel corrosion inhibitor and surfactant in hydrochloric acid. *Corros Sci* 82:265–270
 31. Popova A, Christov M, Vasilev A (2015) Mono- and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part III: influence of the temperature on the inhibition process. *Corros Sci* 94:70–75
 32. Fouda AS, El-Kaabi SS, Mohamed AK (1990) Substituted phenyl *N*-phenylcarbamates as corrosion inhibitors for iron in HCl. *Corros Prev Control* 16:164–167
 33. Bentiss F, Lagrenee M, Traisnel M, Lornez JC (1999) The corrosion inhibition of mild steel in acidic media by a new triazole derivatives. *Corros Sci* 41:789–803
 34. Mc Caaffery E (1979) Corrosion control by coatings. Science Press, Princeton
 35. Al-Anadoui B, Elnizami F, Ateya B (1988) Extended abstract of the electrochemical society fall meeting, Chicago, p 188
 36. Borkirs JO'M, Swinkless DAJ (1964) Adsorption of *n*-decylamine on solid metal electrodes. *J Electrochem Soc* 111:136
 37. Khamis E, Ameer MA, Al-Andis NM, Al-Senani G (2000) Effect of thiosemicarbazones on corrosion of steel in phosphoric acid produced by wet process. *Corrosion* 56(2):127–138
 38. El-Awady YA, Ahmed AI (1985) Effect of temperature and inhibitors on the corrosion of aluminum in 2 N HCl solution: a kinetic study. *J Ind Chem* 24A:601–605
 39. Fouda AS, Al-Sarawy AA, El-Katori EE (2006) Pyrazolone derivatives as corrosion inhibitors for C-steel in hydrochloric acid solution. *Desalination* 201:1–13
 40. Aramaki K, Hackerman M (1969) Inhibition mechanism of medium-sized polymethyleneimine. *J Electrochem Soc* 116(5):568–574
 41. Quartarone G, Moretti G, Tassan A, Zingales A (1994) Inhibition of mild steel corrosion in 1 N sulphuric acid through indole. *Werkst Korros* 45:641–647
 42. Samkarapapaavinasam S, Ahmed MF (1992) Benzenethiols as inhibitors for the corrosion of copper. *J Appl Electrochem* 22:390–395
 43. Schweinsberg D, George G, Kuruppu Nanayakkara A, Steinert D (1988) Inhibitive effects on the aqueous acid corrosion of iron and steel. *Corros Sci* 28:33–42
 44. Fouda AS, Moussa MN, Taha FI, El-Neanaa AI (1986) the role of some thiosemicarbazide derivatives in the corrosion inhibition of Al in HCl. *Corros Sci* 26:719–726
 45. Abdallah M, Helal EA, Fouda AS (2006) Antipyrimidine derivatives as inhibitors for corrosion of 1018 carbon steel in nitric acid solution. *Corros Sci* 48:1639–1654
 46. Donahu FM, Nobe K (1965) Theory of organic corrosion inhibitors. *J Electrochem Soc* 112:886–891
 47. Vasseghi S, Nobe K (1979) Thiazole, benzotriazole and naphthotriazole as corrosion inhibitors for copper. *Corrosion* 35:300–303
 48. Szklavska-Smialowska Z, Kaminski M (1973) Effect of various substituted in thiophene on the inhibitor efficiency. *Corros Sci* 13:1–10