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Macro Heterocyclic Compounds as Corrosion Inhibitors for304 Stainless Steel in Hydrochloric Acid Solutions

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ABSTRACT

The corrosion behavior of stainless steel (SS) type 304 in 1 M HCl and at different temperatures (25 ^{o}C - 55 ^{o}C) in presence of different concentrations of heterocyclic organic compounds was studied using chemical (weight loss) and electrochemical (potentiodynamic polarization and electrochemical impedance spectroscopy) techniques. The polarization curves reveal that these investigated compounds act as mixed type inhibitors. Adsorption of these inhibitors on SS surface was found to obey the Langmuir adsorption isotherm. Results show that the rate of corrosion of SS increased with increasing temperature over the range (25 ^{o}C - 55 ^{o}C) both in the presence and the inhibitors and in their absence and decreases with increasing inhibitor concentration. This indicates that these compounds were assumed to occur via physical adsorption on the steel surface. Activation energies in the presence and absence of these investigated compounds were obtained by measuring the temperature dependence of the corrosion current. The reactivity of these compounds was analyzed through theoretical calculations based on semiempirical theory to explain the different efficiency of these compounds as corrosion inhibitors.

Introduction

Stainless steels are used in various applications due to their good resistance to general corrosion, high strength, workability and weldability. 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 [1-6]. There has been an increased utilization of heterocyclic organic compounds in acid corrosion inhibition [7-11]. 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 [12–16].

Experimental Methods

Materials and solution

The experiments were performed with type 304 stainless steel 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. SS Type 304 specimens were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), ultrasonically degreased in acetone [17], 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 of the investigated chemical compounds are shown below:

Methods

Weight loss technique

The reaction basin used in this method was a 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 nearly 20 x 20 x 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 basin, and under the surface of the test solution by about 1 cm. 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 and the value of weight loss in mg has been reported.

Electrochemical technique

Three electrochemical techniques have been employed for studying the inhibition SS of type 304 corrosion in the presence and absence of the investigated compounds: a) Potentiodynamic polarization technique b) Electrochemical impedance spectroscopy (EIS) and c) Electrochemical modulation technique (EFM).

Potentiodynamic polarization method

Stainless steel Type 304 strips with an exposed area of 1 cm were used. Measurements were carried out in a standard glass three-electrode cell with a capacity of 250 ml for polarization curves. A constant quantity of the test solution (100 ml) was taken in the polarization cell. The counter and the reference electrodes are platinum and saturated calomel (SCE), respectively. A time interval of about 800 second was given for the system to attain a steady state and the open circuit potential (OCP) was noted. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically

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from –150 to 150 mV with scanning rate 0.5 mVs^{-1} by using Volta Lab PGZ100. and a personal computer with VoltaMaster 4 version 7.08 software for calculations. Solutions were not deaerated to make the conditions identical to weight loss measurements. All the experiments were carried out at different temperatures 25, 35, 45 and 55 ± 1 ^{o}C by using ultra circulating thermostat. The procedure adopted for the polarization measurements was the same as described elsewhere [18].

Electrochemical impedance spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) measurements were performed by using the three-electrode glass cell assembly as that used in polarization experiments. The EIS spectra were recorded at open circuit potential, OCP after immersion the electrode for 800 seconds. The AC signal was 0.5 mV pick to pick and the frequency range studied was between 100 kHz and 0.1 Hz by using Potentiostat/Galvanostat (Gamry PCI 300/4) and a personal computer with EIS 300 soft ware for calculations.

Results and discussion

Corrosion behavior of SS type 304 by weight loss technique

Studying of the corrosion behavior of type 304 stainless steel in 1.0 M HCl in the presence and absence of compound (A) at 25 ^{o}C is represented in Figure 1. As shown from this figure, by increasing the concentration of these derivatives, the weight loss of type 304 stainless steel samples were decreased. This means that the presence of these compounds retards the corrosion of SS type 304 in 1.0 M HCl or in other words, these derivatives act as inhibitors. The values of percentage inhibition of investigated compounds are given in Table 1. From this table, the order of the inhibition efficiencies of the investigated compounds is as follows: A > B > C. It is obvious that the inhibition efficiency increases with increasing the concentration the investigated compounds.

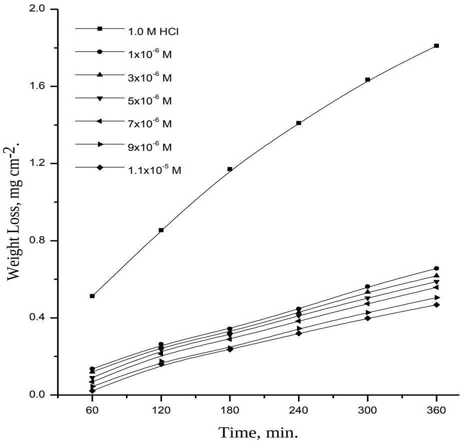


Figure 1. Weight loss - time curves for the corrosion of type 304 stainless steel in 1.0 M HCl in the absence and presence of different concentrations of inhibitor (A) at 25 ^{o}C

Adsorption isotherm

The adsorption of an organic adsorbate on the surface of a metal is regarded as a substitutional adsorption processes between the organic compound in aqueous phase, org(aq), and the water molecule adsorbed on the electrode surface [19, 20]:

$$Org._{(aq.)} + nH_2O_{(S)} ===== Org._{(S)} + nH_2O_{(aq.)} \quad (1)$$

Where n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. According to Bockris and Swinkless [21], (n) is assumed to be independent of coverage or charge of electrode. Clearly, the value of (n) will depends on the cross-sectional area of organic molecule with respect to that of water molecule. At equilibrium the chemical potential (θ) 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, some being empirical and other theoretical.The simplest theoretical equation is that due to Langmuir and given by the equation [22].

$$f(\theta, x)\ \exp(-a, \theta) = KC \quad (2)$$

Where f (θ, x) is the configurationally factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm, (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 equilibrium constant of the adsorption process, K, which is related to the standard free energy of adsorption (ΔG^{o}_{ads}) by:

$$K=1/55.5[\exp- \Delta G^{o}_{ads} /RT] \quad (3)$$

where R is the universal gas constant and T is the absolute temperature. Plots of C/θ vs. C (Langmuir's isotherm) for adsorption of the investigated compounds on the surface of type 304 stainless steel in 1 M HCl at 25 ^{o}C are shown in Figure 2. The data gave straight lines with slopes equal to nearly 1 indicating that Langmuir's isotherm is valid for these systems. On the other hand, it is found that the kinetic-thermodynamic model of El- Awady et al. [23]:

$$\log [\theta/(1-\theta)] = \log K' + y \log C \quad (4)$$

Is valid to operate the present adsorption data.The equilibrium constant of adsorption $K = K'^{(1/y)}$, 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 $\log [\theta/(1-\theta)]$ against log C at 25 ^{o}C a straight line relationships were obtained (Figure 3) suggesting the validity of this model for all cases studied. The calculated values of 1/y, K and ΔG^{o}_{ads} are given in Table 2. Inspection of the data of this table shows that the large values of ΔG^{o}_{ads} 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 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^{o}_{ads} 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^{o}_{ads} so the order of inhibition efficiencies is as follows: A > B > C.

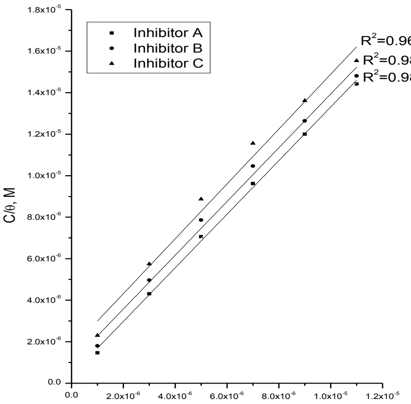


Figure 2. Langmuir adsorption isotherm plotted as (C/θ) vs. concentration of all used inhibitors for the corrosion of 304 stainless steel in 1 M HCl at 25 ^{o}C as obtained from weight loss measurements

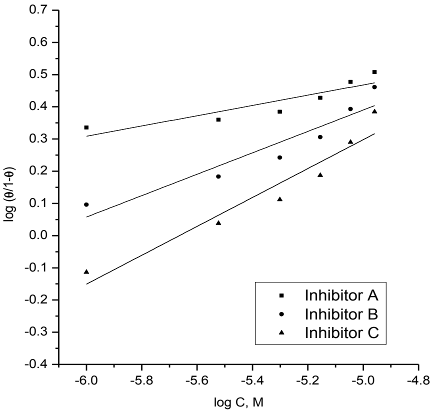


Figure 3. El-Awady kinetic model plotted as log (□/1-□□) vs. log concentration of the investigated compounds for the corrosion of 304 stainless steel in 1 M HCl at 25 °C as obtained from weight loss measurements

Study the corrosion behavior of 304 SS by Potentiodynamic polarization technique

Electrochemical technique is based on current and potential measurements. According to the choice of the technique accurate and confidential data, concerning the corrosion process can be obtained. Potentiodynamic polarization curves of 304 stainless steel in 1 M HCl in the absence and presence of different concentrations of compound (A) at 25 °C is illustrated in Figure 4. The numerical values of the variation of corrosion current density ($i_{corr.}$), corrosion potential ($E_{corr.}$), Tafel slopes (β_a and β_c), corrosion rate, degree of surface coverage (θ) and % inhibition efficiency with the concentrations of compound (A) are given in Table 3. The results of this table indicate that by increasing the concentration of inhibitor, the i_{corr} decreases and hence, % inhibition increases. Table 4 represents the % inhibition of the investigated compounds as determined from potentiodynamic polarization technique. The results of this table follow the order: A > B > C.

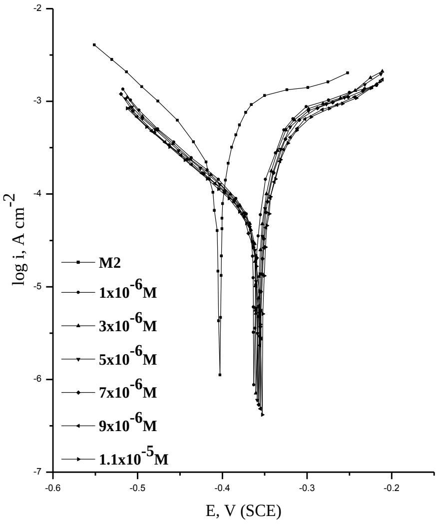


Figure 4. Potentiodynamic polarization curves of 304 stainless steel in 1.0 M HCl in the absence and presence of different concentrations of inhibitor (A) at 25 °C

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 elsewhere [24, 25]. Table 5 shows the influence of 0.01 M KI on inhibition efficiency of various concentrations of the investigated compounds for 304 stainless steel using potentiodynamic polarization technique. It can be seen from this table that the addition of KI increases the inhibition efficiency of the investigated compounds for 304 stainless steel. Figure 5 represents the potentiodynamic polarization curves of type 304 stainless steel in1 M HCl in the absence and presence of $1x10^{-2}$ M KI and different concentrations 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 component stabilized the adsorption of the investigated compounds on the steel surface. This stabilization may be caused by the interaction between inhibitor molecule and iodide ions. Thus, the interaction enhances the inhibition efficiency to a considerable extent due to the increase of the surface coverage in the presence of iodide ions. Figure 6 represents the plots of synergism parameters S□ of KI versus the concentrations of the investigated compounds at 25 °C.

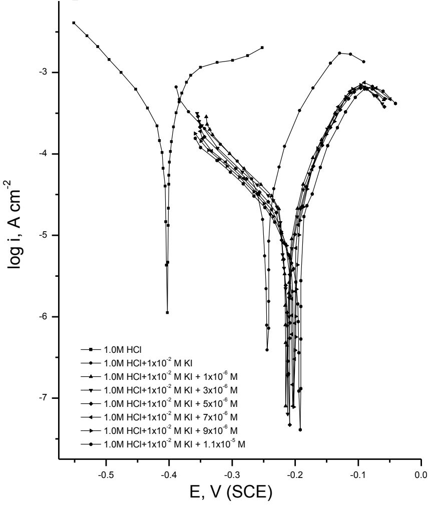


Figure 5. Potentiodynamic polarization curves of 304 stainless steel in 1 M HCl in the absence and presence of $1x10^{-2}$ M KI and different concentrations of inhibitor (A) at 25 °C

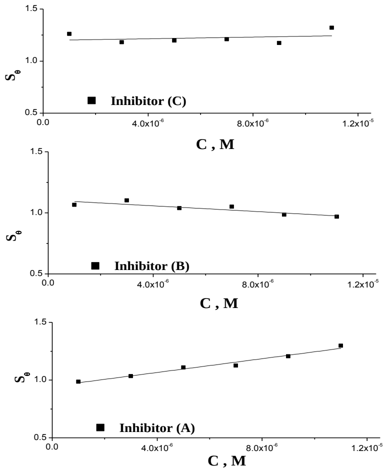


Figure 6. Plots of synergism parameters S_θ of KI versus the concentrations of the investigated compounds at 25 °C

Effect of temperature and 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, the % inhibition is decreased by increasing the temperature. This indicates that these derivatives are adsorbed on type 304 stainless steel surface physically, also the order of inhibition efficiency decreased as follows: A > B > C. The increase in the temperature has a reverse relationship with the percentage efficiency this means that the adsorption of the investigated compounds on the metal surface is physical. Figure 7 represents plots of the log rate vs. 1/T and Figure 8 shows the relation between log (rate/T) vs. 1/T data. The calculated values of the apparent activation energy, Ea^*, activation entropies, ΔS^*, and activation enthalpies, □H^*, are given in Table 6. Generally we can say the nature and the concentration of electrolyte affect greatly the activation energy for the corrosion process. The results which are presented in Table 6 show that the enthalpy of activation is all positive. The positive sign of the enthalpy reflects the endothermic nature of the stainless steel dissolution process [26]. 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 on going from reactants to the activated complex [27].

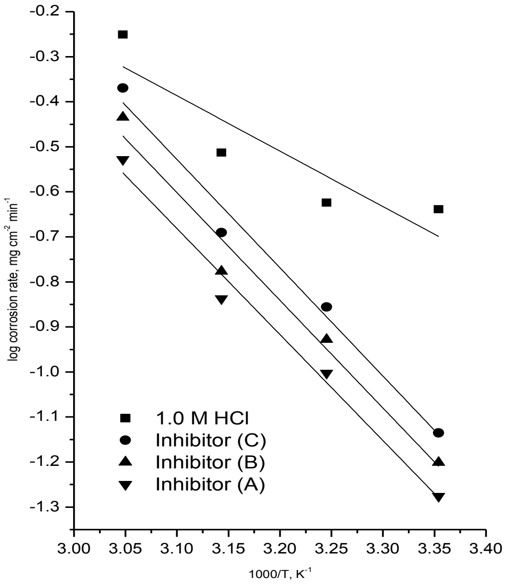


Figure 7. Plots of log corrosion rate vs. (1000/T) for 304 stainless steel dissolution in 1 M HCl in absence and presence of $1.1x10^{-5}$ M of all used inhibitor.

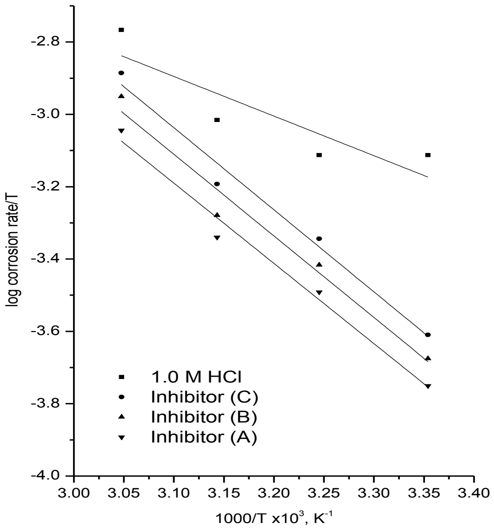


Figure 8. Plots of log (corrosion rate/T) vs. (1000/T) for 304 stainless steel dissolution in 1 M HCl in absence and presence of $1.1x10^{-5}$ M of all used inhibitors

Electrochemical Impedance spectroscopy (EIS)

The corrosion behavior of 304 SS in 1 M HCl solution in the absence and presence of different concentrations of the investigated compounds was examined by the EIS technique at 25 ±1 °C. Figures (9, 10) show the Nyquist and Bode plots respectively for type 304 SS in 1.0 M HCl solution in the absence and presence of different concentrations 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)
- The capacity of double layer C_{dl} which is defined as:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \tag{5}$$

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

$$\theta = \left(1 - \frac{R^o_{ct}}{R_{ct}}\right) \tag{6}$$

$$\%IE = \left(1 - \frac{R^o_{ct}}{R_{ct}}\right) \times 100 \tag{7}$$

where R^o_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of different concentrations of inhibitor, respectively. The associated with the diagrams impedance are given in Table 7.

Table 8 shows the inhibition efficiencies of different concentrations of the investigated inhibitors for the corrosion of type 304 stainless steel in 1M HCl at 25 °C as obtained from electrochemical impedance spectroscopy. From the impedance data given in Tables (7, 8), we conclude that: The value of R_{ct} increases with the increasing the concentration of the inhibitors and hence, the increase in the corrosion inhibition efficiency in acidic solution.

- As the impedance diagram obtained has a semicircle appearance, it shows that the corrosion of type 304 SS is mainly controlled by a charge transfer process.
- 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 type 304 SS surface.
- The %IE obtained from EIS measurements are nearly close to those obtained from polarization and weight loss methods. The order of inhibition efficiency obtained from EIS measurements is: A > B > C.
- G. 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:
- 1) Electrostatic attraction between charged molecules and charged metal.
- 2) Interaction of unshared electrons pairs in the molecule with the metal.
- 3) Interaction of π electrons with the metal.
- 4) A combination of the above [28].

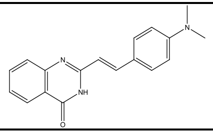
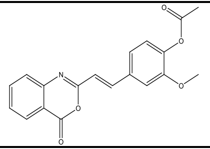
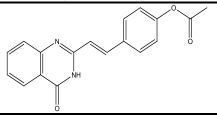
Inh.	Name	Structure	M. FW.	Mol.Wt.
A	(E)-2-(4-(dimethylamino)styryl)quinazolin-4(3H)-one		$C_{18}H_{17}N_3O$	291.35
B	(E)-2-methoxy-4-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)vinyl)phenyl acetate		$C_{19}H_{15}NO_5$	337.33
C	(E)-4-(2-(4-oxo-3,4-dihydroquinazolin-2-yl)vinyl)phenyl acetate		$C_{18}H_{14}N_2O_3$	306.32

Table 1. Inhibition efficiency of investigated compounds at different concentrations as determined from weight loss method at 25°C Duration of the experiment: 240 min immersion in 1M HCl solution

[Inhibitor],M	% IE		
	A	B	C
$1x10^{-6}$	68.4	55.5	43.5
$3x10^{-6}$	69.6	60.4	52.2
$5x10^{-6}$	70.8	63.6	56.4
$7x10^{-6}$	72.8	66.9	60.6
$9x10^{-6}$	75.0	71.2	66.1
$11x10^{-6}$	76.3	74.3	70.8

Table 2. Number of active sites (1/y), slopes of Langmuir isotherms lines, inhibitors' equilibrium constants (K), and free energy of adsorption ($\Delta G^o_{ads.}$) for all used inhibitors obtained from weight loss measurements at 25 °C

Inh.	Kinetic model			Langmuir Isotherm		
	1/y	K x 10^5 M^{-1}	$-\Delta G^o_{ads.}$ kJ mol^{-1}	Slope	K x 10^4 M^{-1}	$-\Delta G^o_{ads.}$ 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

Table 3. Effect of concentrations of inhibitor (A) on the electrochemical parameters of 304 stainless steel in 1 M HCl at 25 °C.

[Inh.], M	$-E_{corr}$ mV	icorr μA cm^{-2}	$-ß_c$ mV dec^{-1}	$ß_a$ mV dec^{-1}	CR mm y^{-1}	θ	IE%
0.0	396	220.4	95	86	2.517	----	----
$1x10^{-6}$	363	66.0	134	70	0.754	0.701	70.1
$3x10^{-6}$	363	63.1	135	70	0.721	0.714	71.4
$5x10^{-6}$	361	60.3	136	70	0.688	0.727	72.7
$7x10^{-6}$	361	55.3	137	71	0.631	0.749	74.9
$9x10^{-6}$	360	52.7	135	71	0.601	0.761	76.1
$1.1x10^{-5}$	359	50.8	136	71	0.580	0.770	77.0

Table 4. Inhibition efficiency at different concentrations of the inhibitors as determined by Potentiodynamic polarization technique at 25 °C

[Inhibitor],M	% IE		
	A	B	C
$1x10^{-6}$	70.1	45.5	54.5
$3x10^{-6}$	71.4	54.1	59.2
$5x10^{-6}$	72.7	58.4	65.2
$7x10^{-6}$	74.9	61.4	67.3
$9x10^{-6}$	76.1	65.3	70.7
$11x10^{-6}$	77.0	68.1	72.6

Table 5. Inhibition efficiencies at different concentrations of inhibitors in presence of $1x10^{-2}$M KI as determined by Potentiodynamic polarization at 25 °C

[Inhibitor], M	% IE		
	A	B	C
$1x10^{-6}$	94.5	92.2	92.2
$3x10^{-6}$	95.0	93.3	93.0
$5x10^{-6}$	95.5	93.9	93.7
$7x10^{-6}$	96.0	94.3	94.2
$9x10^{-6}$	96.4	94.6	94.6
$11x10^{-6}$	96.8	94.9	95.6

Table 6. Activation energy and thermodynamic activation parameters for dissolution of SS type 304 in 1.0 M HCl in the absence and presence of $1.1\text{x}10^{-5}$ M of investigated inhibitors at different temperatures

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

Table 7. Electrochemical kinetic parameters obtained by EIS technique for the dissolution of 304 SS in 1 M HCl in the absence and presence of different concentrations of the investigated inhibitors at 25 °C

Inh.	[Inh], M	C_{dl} (μF cm^{-2})	-phase (deg)	R_{ct} (Ω cm^2)	R_p(Ω cm^2
1.0 M HCl	-----	235.3	56.7	150.2	137.8
A	$5\text{x}10^{-6}$	162.4	67.6	390.0	325.8
	$7\text{x}10^{-6}$	147.1	66.3	430.7	343.9
	$9\text{x}10^{-6}$	111.2	66.8	453.1	372.8
	$1.1\text{x}10^{-5}$	108.3	64.9	584.9	459.7
B	$5\text{x}10^{-6}$	184.7	66.0	343.1	289.8
	$7\text{x}10^{-6}$	159.2	67.3	397.9	333
	$9\text{x}10^{-6}$	140.2	67.2	451.8	369.4
	$1.1\text{x}10^{-5}$	119.8	69.5	528.8	422.2
C	$5\text{x}10^{-6}$	185.0	68.5	315.5	282.4
	$7\text{x}10^{-6}$	179.7	66.2	352.6	296.7
	$9\text{x}10^{-6}$	171.2	66.9	370.0	303
	$1.1\text{x}10^{-5}$	122.3	69.7	517.9	420.8

Table 8. The inhibition efficiencies of different concentrations of the investigated inhibitors for the corrosion of 304 SS in 1 M HCl at 25 °C as obtained from electrochemical impedance spectroscopy

[Inhibitor], M	% IE		
	A	B	C
$5\text{x}10^{-6}$	61.5	56.2	52.4
$7\text{x}10^{-6}$	65.1	62.3	57.4
$9\text{x}10^{-6}$	66.9	66.8	59.4
$11\text{x}10^{-6}$	74.3	71.6	71.0

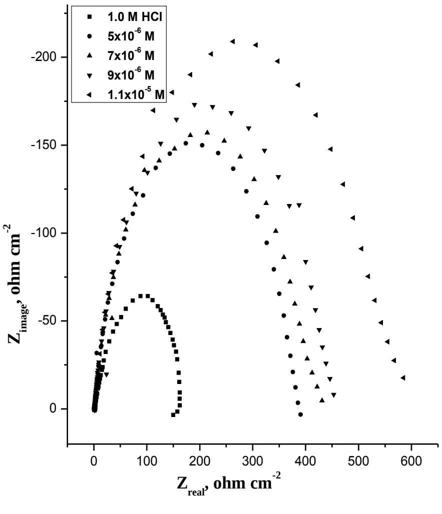


Figure 9. The Nyquist plots for the corrosion of 304 SS in 1M HCl in the absence and presence of different concentrations of inhibitor (A) at 25°C

Concerning inhibitors, the inhibition efficiency depends on several factors; such as (i) the number of adsorption sites and their charge density, (ii) molecular size, heat of hydrogenation, (iii) mode of interaction with the metal surface, and (iv)the formation metallic complexes [29]. 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.

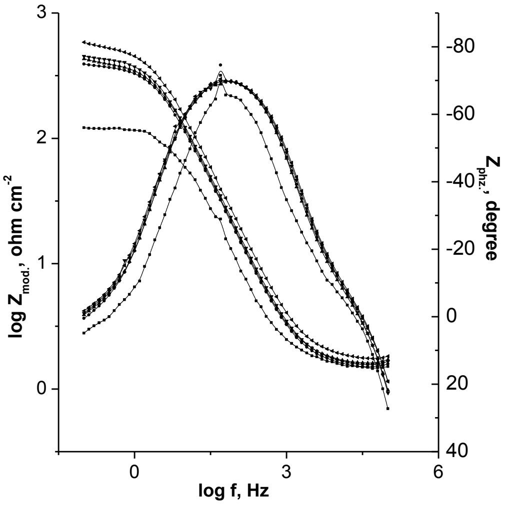


Figure 10. The Bode plots for the dissolution of 304 SS in 1.0 M HCl in the absence and presence of different concentrations of inhibitor (A) at 25 °C

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 inhibition efficiency 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 towards the π-electron clouds of the ring system [30]. 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 inhibition efficiency of organic compounds with their Hammett constituent constants [31]. The LFER or Hammett relation is given by [32, 33]

$$\log R = -\rho\sigma \qquad (8)$$

where ρ is the reaction constant. 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 (rate of corrosion) or % inhibition vs. σ is ρ, and its sign indicates whether the process is inhibited by an increase or decrease of 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 increase the electron density of the ring and increase 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. Compounds (B) comes after compound (A) in inhibition efficiency because it contains an acetyl group ($-COOCH_3$) 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 (N > 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).

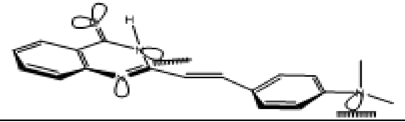
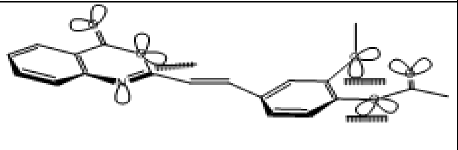
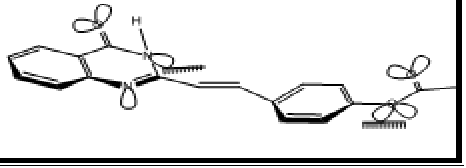
Inhibitor	Skeletal representation
A	
B	
C	

Figure 11. Skeletal representation of the mode of adsorption of the investigated compounds on the metal surface

Conclusions

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

References

[1] P.R.P. Rodrinves, I.V. Aoki, A.H.P. DeAndrade, E. De Oliveria, S.M.L. Agostinho, Effect of benzotriazole on electrochemical and corrosion behaviour of type 304 stainless steel in 2M sulphuric acid solution, Br. Corros. J. 31, 305-308, (4) (1996).

[2] A. Kumor, S.P. Borthakur, H.C. Dhawan, Inhibitive action of some mercaptotriazoles towards the corrosion of Fe-Cr-Ni steel in sulphuric acid, Bull. Electrochem. 15, 63-66, (2) (1999).

[3] X.L. Cheng, H.Y. Ma, S.H. Chen, R. Yn, X. Chen, Z.M. Yao, Corrosion of stainless steels in acid solutions with organic sulfur-containing compounds, Corros. Sci. 41, 321-333, (1999).

[4] R. Agrawal, T.K.G. Namboodhiri, The inhibition of corrosion and hydrogen embrittlement of AISI 410 stainless steel, J. Appl. Electrochem. 22, 383-389, (1992).

[5] M. Abdallah, Rhodanine azosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution, Corros. Sci. 44, 717-728, (2002).

[6] I.L. Rozenfeld, Corrosion Inhibitors, Mc-Graw Hill, 1981, New York.

[7] Z. Jiang, J. Wang, Q. Hu and S. Huang, The influence of 1-(2-pyridylazo)-2-naphthol (PAN) on the corrosion of titanium in 10 N sulfuric acid solution, Corr. Sci., 37, 1245-1252, (1995).

[8] M. Ajmal, A.S. Mideen and M.A. Quraishi, 2-hydrazino-6-methyl-benzothiazole as an effective inhibitor for the corrosion of mild steel in acidic solutions, Corr. Sci., 36, 79-84, (1994).

[9] S.N. Raicheva, B. Aleksiev and E.I. Sokolova, On the corrosion characterization of titanium nitride in sulfuric acid solution, Corr. Sci., 34, 343-347, (1993).

[10] E. Stupnisek-Lisac and Z. Ademovic, 8th European Symp. Corrosion Inhibitors, Ferrara, Italy, 1995, p. 257.

[11] M.A. Quraishi, 8th European Symp. Corrosion Inhibitors, Ferrara, Italy, 1995, p. 277.

[12] F. Bentiss, M. Traisnel, N. Choibi, B. Mernavi, H. Vezin, M. Lagrenee, Anodic film growth on InP in sodium tungstate, Corros. Sci. 44, 2161-2170, (10) (2002).

[13] J.G.N. Thomas, Proceedings of the Fifth European Symposium on Corrosion Inhibitors, vol. V, Suppl. No. 8, Ann University, Ferrara, NS Sez., 1980, p. 453.

[14] A.M. Gad Allah, M.M. Hefny, S.A. Salih, M.S. El-Basiouny, Corrosion Inhibition of Zinc in HCl Solution by Several Pyrazole Derivatives, Corrosion 45, 574-578, (7) (1989).

[15] E. Stupnise Ktisac, M. Metikos-Hukovic, D. Lencic, J.Vorkapic-Furac, K. Berkovic, Structural Investigation of N-Arylpyrroles as Iron Corrosion Inhibitors in Hydrochloric Acid, Corrosion 48, 924-930, (11) (1992).

[16] A.J. Szyproniski, Relationship between chemical structure of imidazoline inhibitors and their effectiveness against hydrogen sulphide corrosion of steels, Br. Corros. J. 35, 155-160, (2) (2000).

[17] A.S. Fouda, S.S. El-Kaabi and A.K. Mohamed, Substituted phenyl N-phenylcarbamates as corrosion inhibitors for iron in HCl, Corrosion Prevention and Control, 164 (1990).

[18] F. Bentiss, M. Lagrenee, M. Traisnel, J.C. Lornez, The corrosion inhibition of mild steel in acidic media by a new triazole derivatives, Corros. Sci. 41, 789-803, (1999).

[19] E. McCaaffery, ‘‘Corrosion Control by Coatings”, Science press, Princeton, 1979.

[20] B. Al-Anadoui, F. Elnizami, B. Ateya, Extended Abstract of the Electrochemical Society Fall Meeting, Chicago, 1988, pp. 188.

[21] J.O’M. Borkirs, D.A.J. Swinkless, Adsorption of n-Decylamine on Solid Metal Electrodes, J. Electrochem. Soc. 111, 736-743 (1964).

[22] E. Khamis, M.A. Ameer, N.M. Al-Andis, G. Al-Senani, Effect of thiosemicarbazones on corrosion of steel in phosphoric acid produced by wet process, Corrosion 56, 127-138, (2) (2000).

[23] Y.A. El-Awady, A.I. Ahmed, Effect of temperature and inhibitors on the corrosion of aluminum in 2N HCl solution: a kinetic study, J. Ind. Chem. 24A, 601, (1985).

[24] E. Khamis, E.S.H. El-Ashry, A.K. Ibrahim, Synergistic action of vinyl triphenylphosphonium bromide with various anions on corrosion of steel, Br. Corros. J. 35, 150-154, (2000).

[25] A.S. Fouda, A.A. Al-Sarawy, E.E. El-Katori, Pyrazolone derivatives as corrosion inhibitors for C-steel in hydrochloric acid solution, Desalination 201, 1-13, (2006).

[26] G. Quartarone, G. Moretti, A. Tassan, A. Zingales, Inhibition of mild steel corrosion in 1 N sulphuric acid through indole, Werkst. Korrosion 45 (1994) 641-647

[27] S. Samkarapapaavinasam, M.F. Ahmed, Benzenethiols as inhibitors for the corrosion of copper, J. Appl. Electrochem. 22, 390-395, (1992).

[28] D. Schweinsberg, G. George, A. Kuruppu Nanayakkara, D. Steinert, Inhibitive effects on the aqueous acid corrosion of iron and steel, Corros.Sci., 28, 33-42, (1988).

[29] A.S.Fouda, M.N.Moussa, F.I.Taha and A.I.El-Neanaa, The role of some thiosemicarbazide derivatives in the corrosion inhibition of Al in HCl, Corros.Sci.,26, 719-726, (1986).

[30] M. Abdallah, E.A. Helal, A.S. Fouda, Antipyimidine derivatives as inhibitors for corrosion of 1018 carbon steel in nitric acid solution, Corros. Sci. 48, 1639-1654, (2006).

[31] F.M. Donahu, K. Nobe, Theory of Organic Corrosion Inhibitors, J. Electrochem. Soc. 112, 886-891, (1965).

[32] S. Vasseghi, K. Nobe, The Effect of Substituted Purines on the Corrosion Behavior of Iron, Corrosion 35, 300-303, (1979).

[33] Z. Szklavska-Smialowska, M. Kaminski, Effect of various substituted in thiophene on the inhibitor efficiency, Corros. Sci. 13, 1-10, (1973).