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Some thiophene derivatives as inhibitors for the corrosion of 304 SS in acidic media

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ABSTRACT

The inhibitive effect of 2-cyano-3-hydroxy-4(Ar) -5- anilino thiophene derivatives on the corrosion of 304 SS in 3 M HCl solution has been investigated by weight loss, galvanostatic polarization and potentiodynamic anodic polarization techniques. The results indicate that these compounds act as inhibitors retarding the anodic and cathodic corrosion reactions. The presence of inhibitors does not change the mechanism of either hydrogen evolution reaction or SS dissolution. Activation energy and some thermodynamic parameters were calculated and discussed. These compounds are mixed type inhibitors in the acid solution, and their adsorption on SS surface is found to obey the Temkin adsorption isotherm. The experimental results suggested that the % inhibition of these thiophene derivatives increases with the increase in inhibitor concentration and decreases with the increase in temperature of the medium. The synergistic parameter (S) was calculated and it was found that its value is greater than unity, which indicates that the enhanced inhibition efficiency caused by the addition of I^-, SCN^- and Br^- is only due to synergistic effect. Relationship between molecular structure and their inhibition efficiency was elucidated by quantum chemical calculations using the semi-empirical self consistent methods (SCF).

KEYWORDS

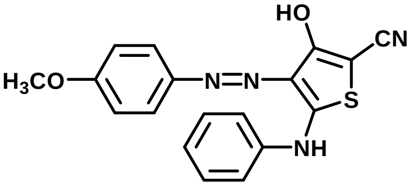
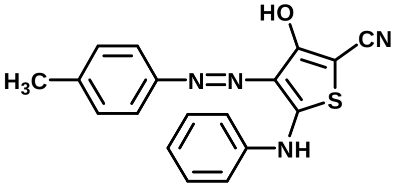
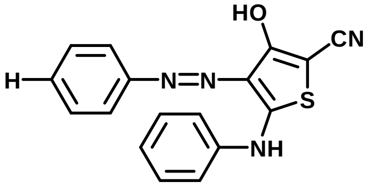
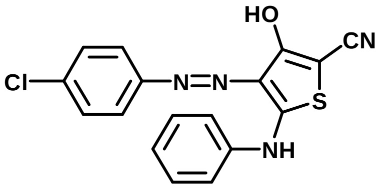
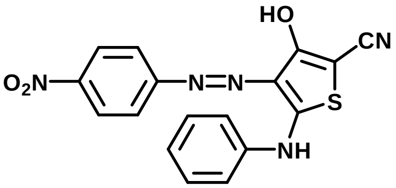
Corrosion;
304 SS;
HCl;
Thiophene derivatives;
Synergistic effect.

INTRODUCTION

The corrosion of stainless steels in acidic solutions has been studied by several authors[1-4]. Iron-chromium alloys are special of interest for many applications because of their excellent resistance to corrosion. The corrosion resistance of stainless steels depends on a very thin oxide film. A passive film occurs rapidly in the presence of oxygen. Although the formation of a film of chromium oxide is effective for protecting stainless steel, the corrosion advances rapidly when localized damage on this passive film occurs[5]. The dissolution of this film in specific aggressive environments is the most common causes of failure of stainless steels.

Many N-heterocyclic compounds with polar groups and / or π-electrons are efficient inhibitors for corrosion in acidic media. The protection action of an inhibitor in metal corrosion is due to the adsorption of this

TABLE 1 The names, molecular formula, structure and molecular weights of the investigated thiophene derivatives are

Comp.	Structures	Names	Molecular formula	molecular weights
I		2-cyano-3-hydroxy-4-(p-anisylazo)-5-anilino thiophene	$C_{18}H_{14}N_4O_2S$	350.1
II		2-cyano-3-hydroxy-4-(p-tolylazo)-5-anilino thiophene	$C_{18}H_{14}N_4OS$	334.1
III		2-cyano-3-hydroxy-4-phenylazo-5-anilino thiophene	$C_{17}H_{12}N_4OS$	320.1
IV		2-cyano-3-hydroxy-4-(p-chlorophenylazo)-5-anilino thiophene	$C_{17}H_{11}N_4OSCl$	354.6
V		2-cyano-3-hydroxy-4-(p-nitrophenylazo)-5-anilino thiophene	$C_{17}H_{11}N_5O_3S$	365.1

inhibitor physically or chemically on the metal surface[6]. Most of the well knows inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms[7,8]. Compounds with functional groups containing hetero atoms which can donate lone pair of electrons are found to be practically useful as inhibitors for corrosion of metals[9]. Previous studies have shown that indole and some of its derivatives display good inhibition properties on corrosion of steel and copper in acidic solutions[10-14]. Some thiophene derivatives were studied as corrosion inhibitors for iron in nitric acid[15] and for AISI 316 SS in HCl solutions[16]. It has been assumed that the first stage in the action mechanism of the inhibitors in the aggressive media is the adsorption of the inhibitors onto the metal surface. The process of adsorption of inhibitors is influenced by the nature and surface charge of the metal, the chemical structure of organic inhibitors, the distribution of charge in molecule, the type of aggressive electrolyte and the type of interaction between organic molecules and the metallic surface[17-21].

The objective of this work was to: i) investigate the inhibition action of some thiophene derivatives towards the corrosion of 304 SS in 3 M HCl using chemical and electrochemical techniques and ii) investigate the effect of addition of some anions and temperature on the corrosion rate and inhibition efficiency.

EXPERIMENTAL

The chemical composition of 304 SS is (weight %): 0.07% C, 2.00% Mn, 0.045% P, 0.030% S, 0.75% Si, 9.0% Ni, 18.0% Cr and the reminder Fe.

Chemical technique (weight loss method)

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 into 2×2×0.1cm. They were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), ultrasonically degreased in acetone[22], rinsed with 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. Precautions were always made to avoid scratching of the specimen during washing after exposure. The weight loss of metal in the corrosive solution is given by:

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

where: W_B is the weight of metal before exposure to the corrosive solution. W_A is the weight of metal after exposure to the corrosive solution.

The percentage inhibition efficiency (IE %) and the degrees of surface coverage (θ) of the investigated molecules were computed by the following equations:

$$\text{IE \%} = [1-(k_{corr(inh)}/\ k_{corr})]\times 100 \qquad (2)$$

$$\theta = [1-(k_{corr(inh)}/\ k_{corr})] \qquad (3)$$

where: k_{corr} and $k_{corr(inh)}$ is the weight loss of metal per unit area in the absence and presence of inhibitors at given time period and temperature respectively.

Electrochemical techniques

SS was a cylindrical rod embedded in araldite with exposed surface of 1.0 cm^2 was employed. Prior to each experiment the surface of 304 SS were mechanically polished with different grades of emery paper, degreased with alkaline solution and rinsed by distilled water. Also a saturated calomel electrode (SCE) and a platinum foil were used as reference and auxiliary electrodes, respectively.

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 and the open circuit potential (OCP) was noted. Both cathodic and anodic polarization curves were recorded galvanostatically using Amel Galvanostat (Model-549) and digital Multimeters (Fluke-73) were used for accurate measurements of potential and current density. Solutions were not dearated to make the conditions identical to weight loss measurements. All the experiments were carried out at 30±1°C by using ultra circulating thermostat.

TABLE 2 : % Inhibition efficiency at different concentrations of the investigated thiophene derivatives for the corrosion of 304 SS in 3M HCl at 30°C

Conc. M	(IE(%))				
	(I)	(II)	(III)	(IV)	(V)
1×10^{-6}	24.0	14.5	15.5	8.8	6.4
3×10^{-6}	27.8	19.3	19.2	15.4	8.7
5×10^{-6}	30.4	24.5	21.9	21.2	13.28
7×10^{-6}	31.8	26.5	24.6	26.1	15.2
9×10^{-6}	32.9	28.1	29.8	31.6	15.9
1.2×10^{-5}	40.9	35.3	34.8	33.4	16.4

Corrosion current density can be determined from polarization curves in different ways. Two methods are, in general, used for the determination of the corrosion current density (I_{corr}). These methods are Stern-Geary[23] method and intercept (Wagner et al., (1938)) method and they are based on anodic and/ or cathodic Tafel curves.

Stern-Geary method used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines of charge transfer controlled corrosion reactions to a point which gives log I_{corr} and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each concentration of inhibitor. Then j_{corr} was subsequently obtained and used for calculation of inhibition efficiency and surface coverage (θ).

$$\text{IE \%} = [1-(j_{corr\ (inh)}/\ j_{corr\ (free)})]\times 100 \qquad (4)$$

$$\theta = [1-(j_{corr\ (inh)}/\ j_{corr\ (free)})] \qquad (5)$$

where: $j_{corr\,(free)}$ is the corrosion current in the absence of inhibitor. $j_{corr\,(inh)}$ is the corrosion current in the presence of inhibitor.

For potentiodynamic anodic polarization study was carried out using Volta Lab (PG 100) with software Voltamaster 4. The examinations of 304 SS potentiodynamically were carried out from -1000 to 1000 mV at scanning rate 1 mV/sec in 3.5% NaCl in the absence and presence of 1×10^{-6}, 3×10^{-6}, 5×10^{-6},

TABLE 3 : Synergistic parameter (S) for various concentrations of all investigated inhibitors in 3M HCl in the presence of 1×10^{-2}M of KI, KSCN and KBr at 30°C from weight loss method

	Conc. M	(S)				
		Compound (I)	Compound (II)	Compound (III)	Compound (IV)	Compound (V)
KI	1×10^{-6}	1.5	1.4	1.2	1.3	1.4
	3×10^{-6}	1.7	1.6	1.2	1.5	1.5
	5×10^{-6}	1.8	1.6	1.3	1.6	1.4
	7×10^{-6}	1.8	1.7	1.4	1.7	1.4
	9×10^{-6}	1.8	1.8	1.5	1.8	1.5
	1.2×10^{-5}	1.8	1.9	1.3	1.5	1.6
KCNS	1×10^{-6}	1.0	1.1	1.5	1.2	1.2
	3×10^{-6}	1.0	1.2	1.1	1.2	1.1
	5×10^{-6}	1.0	1.2	1.1	1.1	1.1
	7×10^{-6}	1.0	1.2	1.1	1.2	1.1
	9×10^{-6}	1.0	1.2	1.2	1.2	1.0
	1.2×10^{-5}	1.0	1.3	0.9	1.0	1.1
KBr	1×10^{-6}	0.9	0.8	0.9	1.0	1.0
	3×10^{-6}	0.9	0.9	0.9	1.1	1.1
	5×10^{-6}	0.9	1.0	0.9	1.1	1.1
	7×10^{-6}	1.0	1.0	1.1	1.2	1.0
	9×10^{-6}	1.0	1.1	1.0	1.3	1.0
	1.2×10^{-5}	1.0	1.3	0.9	1.1	1.1

TABLE 4 : % Inhibition efficiency at various concentrations of all inhibitors in presence of 110^{-2} M KI, KSCN and KBr as determined from weight loss method for the corrosion of 304 SS in 3 M HCl at 30°C

	Conc. M	(IE(%))				
		Compound (I)	Compound (II)	Compound (III)	Compound (IV)	Compound (V)
KI	1×10^{-6}	62.8	60.3	60.3	58.6	53.9
	3×10^{-6}	65.2	61.7	61.7	60.8	55.7
	5×10^{-6}	66.5	63.1	62.9	62.6	57.4
	7×10^{-6}	67.6	65.6	64.9	63.9	59.1
	9×10^{-6}	68.7	68.1	66.4	65.6	63.1
	1.2×10^{-5}	71.5	71.0	70.4	67.6	66.2
KCNS	1×10^{-6}	56.7	51.9	49.5	44.7	49.3
	3×10^{-6}	60.6	59.6	52.9	54.9	53.8
	5×10^{-6}	64.1	62.9	57.7	59.7	56.8
	7×10^{-6}	67.4	64.9	62.0	62.2	58.9
	9×10^{-6}	68.6	67.8	64.8	64.6	61.7
	1.2×10^{-5}	70.2	69.0	67.9	66.3	63.2
KBr	1×10^{-6}	25.8	18.8	15.5	12.8	11.4
	3×10^{-6}	30.7	24.6	23.6	19.4	19.3
	5×10^{-6}	31.6	31.4	26.9	24.1	22.8
	7×10^{-6}	37.8	36.9	37.8	29.8	27.9
	9×10^{-6}	41.8	41.8	34.3	33.8	33.3
	1.2×10^{-5}	51.8	45.9	42.7	41.7	38.1

7×10^{-6}, and 9×10^{-6} and 12×10^{-6} thiophene derivative.

RESULTS AND DISCUSSION

Weight-loss method

Figure 1 shows the weight loss-time curves for 304 SS in 3M HCl in the absence and presence of different concentrations of thiophene derivatives. As shown from this Figure, by increasing the concentration of these compounds, the weight loss of 304 SS samples are decreased. This means that the presence of these compounds retards the corrosion of 304 SS in 3M HCl or in other words, these compounds act as inhibitors.

The linear variation of weight loss with time in uninhibited and inhibited 3M HCl indicates the absence of insoluble surface films during corrosion. In the absence of any surface films, the inhibitors are first adsorbed on to the metal surface and thereafter impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes. The enhancement of inhibition efficiency with increase in inhibitor concentration either could be due to the higher activation energy or to the increase in surface coverage by inhibitor. From the calculated values of %IE given in TABLE 2, the order of the inhibition efficiencies of thiophene derivative compounds is as follow: **(II)** > **(III)** > **(IV)**> **(V)** > **(I)**.

Synergistic parameter

All the experimental results suggest that addition of KI, KSCN, KBr to the corrosive solutions containing various concentrations of the thiophene derivatives significantly increases the inhibition efficiency. This behavior may be attributed to the results of synergistic effect between these anions and thiophene derivatives. The synergistic parameter (S) can be further used to reveal the effect between two compounds[24] Aramaki and Hackerman[25] calculated the synergism parameter S_θ using the following equation.

$$\mathbf{S_\theta = 1- \theta_{1+2} / 1-\theta'_{1+2}} \qquad (6)$$

where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$, θ_1 = surface coverage

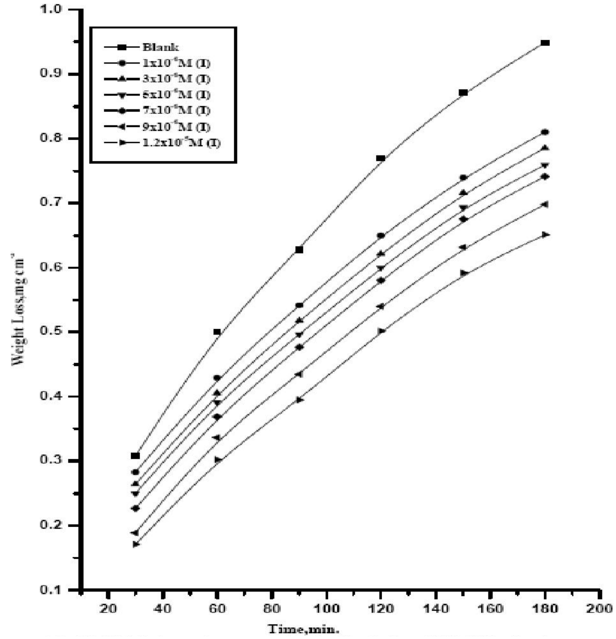


Figure 1 :Weight loss - time curves for the dissolution of 304 SS in the abscence and presence of different concentrations of compound (I) at 30°C

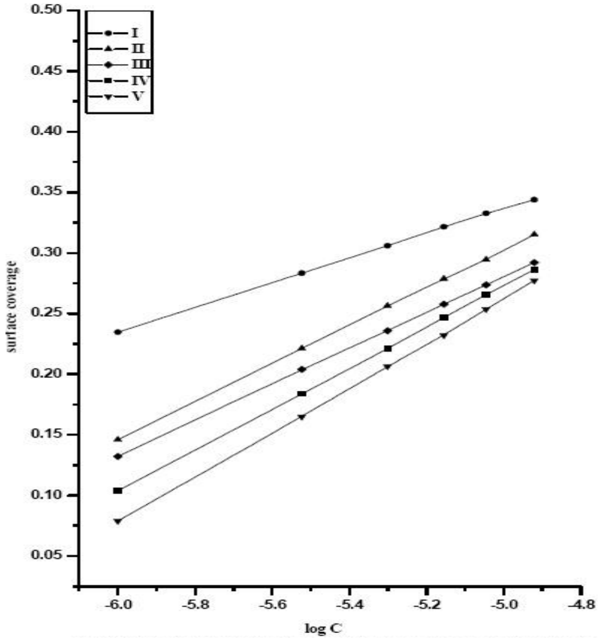


Figure 2 : θ-log C curves for 304 SS in 3M HCl in the presence of all inhibitors from weight loss measurments at 30°C

by anion, θ_2 = surface coverage by cation and θ'_{1+2} = measured surface coverage by both the anion and cation.

Accordingly, S approaches 1 when no interaction between inhibitors exists, while S > 1 points to a synergistic effect. In case S < 1, the antagonistic interaction prevails, this may be attributed to competitive adsorption[26].

The values of S between thiophene derivatives and KI, KSCN, KBr were calculated via eq. (6) and are listed in TABLE 3. As can seen from this TABLE 3, most values of the S are more than unity, which suggests that the improvement in inhibition efficiency is due to a synergistic effect generated by the addition of KI, KSCN, KBr to 3M HCl containing different concentrations of thiophene derivatives, but the maximum synergistic effect presents when the concentration of thiophene derivatives is 1.2×10^{-5} M. It is known that KI would be considered as one of the effective anions for synergistic action within the investigated salts. The synergistic effect depends on the type and concentration of anions. The adsorption ability on the 304 SS surfaces was in the order: KI > KSCN > KBr (TABLE 4). Similar results were obtained by other researchers[27-29].

Obviously, thiophene compounds are nitrogen and sulfur-contain organic compounds, which contains unshared electron pair and π-electrons. So, thiophene derivatives can be adsorbed onto the surface of 304 SS through the transference of lone-pair electrons of nitrogen and sulfur atoms to the d-orbital in iron atom, but in acid solution thiophene compounds may be protonated, leading to positive charge in molecule. It is well known that steel surface contains positive charge due to E_{corr}-$E_{q=0}$ (zero charge potential) > 0[30] in acid solution, thus, it is difficult for positively charged thiophene derivatives to approach the positively charged steel surface because of the electrostatic repulsion. This may be why single thiophene derivatives cannot act as excellent inhibitor for steel corrosion in 3M HCl solution without I^-, SCN^-, Br^- anions. When these anions (I^-, Br^-, SCN^-) are added to 3 M HCl containing thiophene derivatives, firstly, they adsorbed on steel surface turning it negatively charged, thus, the protonated thiophene cations are likely to be adsorbed not only through electrostatic interaction on the steel surface previously covered with these anions but also through the transference of lone-pair electrons of N- and S- atoms to the d-orbital in iron atom. So thiophene cations and (I^-, Br^-, SCN^-) ions can be easily adsorbed onto the steel surface. This may be why the inhibition efficiency in the presence of thiophene derivatives and KI, KSCN, KBr

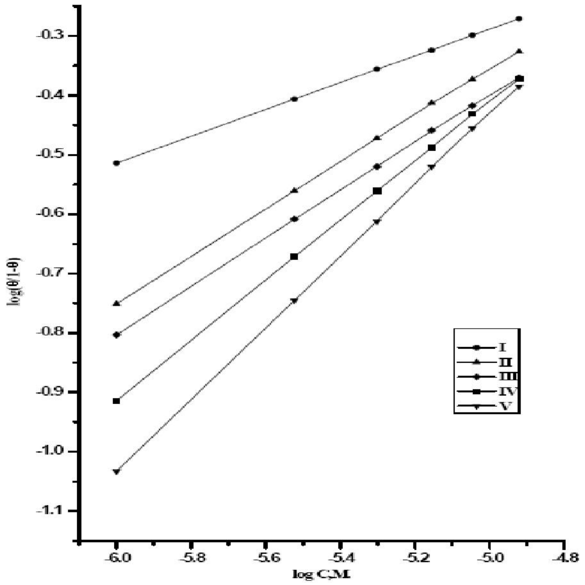


Figure 3 : Curve fitting of corrosion data for 304 SS in 3M HCl in the presence of different concentrations of Thiophene derivatives to kinetic model

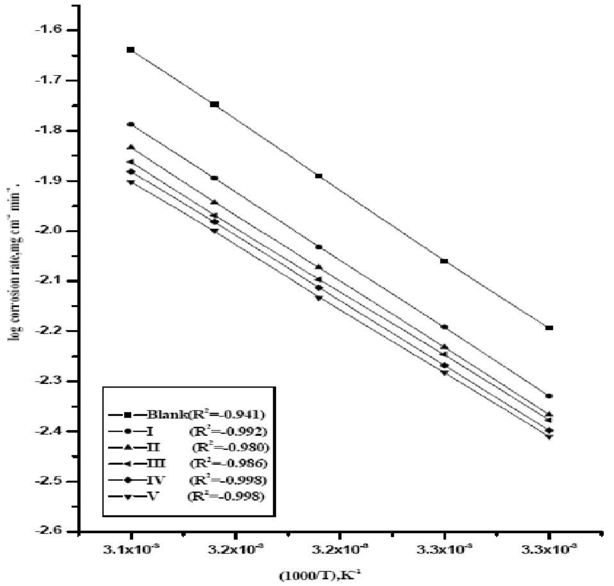


Figure 4 : log corrosion rate vs.1/T curves for 304 SS dissolution in absence and presence of 9×10^{-6}M of inhibitors

is more significantly higher than that in the presence of single thiophene derivatives.

Adorption isotherm

To understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the metal surface must be known. If simple adsorptive behavior is assumed for thiophene derivatives, a direct relationship between inhibition efficiency and surface coverage, θ, of the inhibitor, takes place and weight loss and electrochemical polarization data were used to evaluate the surface coverage values, which are given by eq. 3 & 5.

The surface coverage values (θ) were tested graphically to allow fitting of a suitable adsorption isotherm. The plots of θ vs. log C (Figure 2) yielded straight lines which clearly proving that the adsorption of thiophene derivatives from 3 M HCl solution on 304 SS obeys the Temkin adsorption isotherm where[31]:

$$\mathbf{f(\theta, x)exp(- a, \theta) = KC} \qquad (7)$$

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 (a < 0 means repulsion and a > 0 means attraction) . All adsorption expressions include the equilibrium constant of the adsorption process, K, which is related to the standard free energy of adsorption ($\Delta G°_{ads}$) by:

$$\mathbf{K = (1/55.5) exp (-\Delta G°_{ads}/RT)} \qquad (8)$$

where R is the universal gas constant and T is the absolute temperature.

On the other hand, it is found that the kinetic-thermodynamic model of El-Awady et al.[32]:

$$\mathbf{log (\theta/1-\theta) = log K' + y log C} \qquad (9)$$

Eq. (9) is valid to operate the present adsorption data. The equilibrium constant of adsorption $K = K'^{(1/y)}$, where 1/y is the number of surface active sites occupied by one thiophene derivatives and C is the bulk concentration of the inhibitor. By plotting log (θ/ 1-θ) against log C for the used thiophene derivatives at 30°C a straight line relationships were obtained (Figure 3) suggesting the validity of this model for all cases studied. The values of a, K and $\Delta G°_{ads}$ calculated by Temkin adsorption isotherm and 1/y, K and $\Delta G°_{ads}$ calculated by the kinetic model are given in TABLE 4. Inspection of the data of this table shows that the large values of $\Delta G°_{ads}$ and its negative sign indicate that the adsorption of thiophene derivatives on 304 SS surface is proceeding spontaneously and is accompanied by highly-efficient adsorption. Also, the value of 1/y is more than unity. This means that the given inhibitor molecules will occupy more than one active site. The values of $\Delta G°_{ads}$

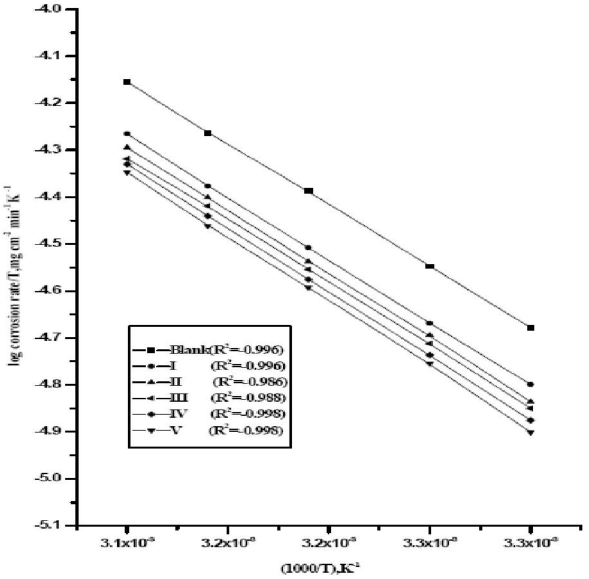


Figure 5 : log corrosion rate/T vs.1/T curves for 304 SS dissolution in the absence and presence of 9×10^{-6}M of inhibitors

TABLE 5 : Inhibitor binding constant (K), free energy of binding ($\Delta G°_{ads}$) lateral interaction parameter (a) and number of active sites (1/y) of all inhibitors (9×10^{-6} M) for the corrosion of 304 SS in 3 M HCl at 30°C

	Temkin			**Kinetic model**		
Inhibitor	**a**	**K×10^{-6}, (M^{-1})**	**-$\Delta G°_{ads}$, (kJ mol^{-1})**	**1/y**	**K×10^{-4} (M^{-1})**	**-$\Delta G°_{ads}$, (kJ mol^{-1})**
(I)	22.6	2.0	58.3	2.0	1.6	40.2
(II)	14.7	8.6	50.3	1.7	2.0	35.0
(III)	15.6	7.9	50.1	2.5	1.2	33.9
(IV)	13.6	4.1	48.4	2.5	1.0	33.3
(V)	12.5	2.7	47.8	4.44	5.6	31.7

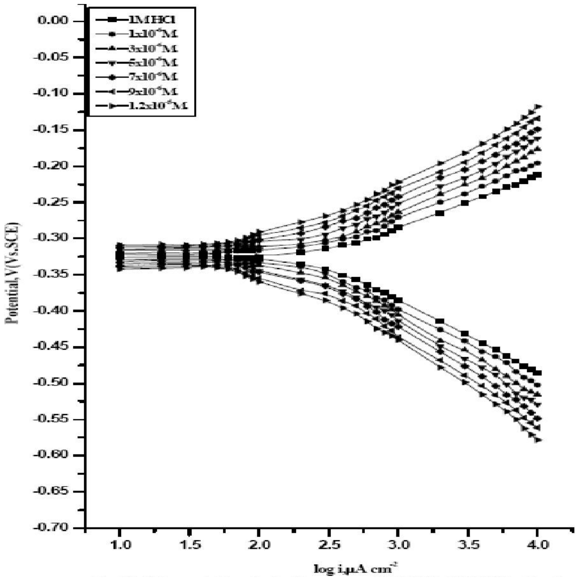


Figure 6 : Galvanostatic polarization curves of 304 SS in 3M HCl in the absence and presence of different concentration of compound (I) at 30°C

TABLE 6 : Activation parameters of the dissolution of 304 SS in 3M HCl in the presence and absence of 9×10^{-6} M investigated compounds

Inhibitor	**Activation Parameters**		
	-E_a^*, (kJ mol^{-1})	**ΔH^*, (kJ mol^{-1})**	**-ΔS^*, (J mol^{-1} K^{-1})**
Blank	52.6	49.96	122.3
(I)	56.8	54.16	111.2
(II)	56.4	53.72	112.0
(III)	55.2	52.52	117.0
(IV)	53.2	50.59	123.9
(V)	53.4	50.64	124.3

obtained from Temkin adsorption isotherm are comparable with those obtained by El-Awady model. From TABLE 3 also we can conclude that the more efficient inhibitor is the one which has the more negative values of ΔG_{ads}, so the inhibition efficiencies is as follows: **(I) > (II) > (III) > (IV) > (V)**.

Effect of temperature

To investigate the mechanism of inhibition and to determine the activation energy of the corrosion process, weight loss curves of 304 SS in 3 M HCl were determined at various temperatures (35 40, 45 and 50°C) in the absence and presence of 1×10^{-6}, 3×10^{-6}, 5×10^{-6}, 7×10^{-6}, 9×10^{-6} and 12×10^{-6} M of thiophene derivatives. The data prove that % inhibition is decreased as the temperature increased, also the order of inhibition efficiency is: **(I) > (II) > (III) > (IV) < (V)**.

Activation parameters of corrosion process

The apparent activation energy E_a^*, the enthalpy of activation ΔH^* and the entropy of activation ΔS^* for the corrosion of 304 SS samples in 3M HCl solutions in the absence and presence of different concentrations of thiophene derivatives were calculated from Arrhenius-type equation:

$$\text{Rate (k)} = A \exp(-E_a^*/RT) \qquad (10)$$

The Eyring equation is:

$$\text{Rate (k)} = \exp(-\Delta G°_{ads}/RT)$$
$$=(RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (11)$$

where A is the frequency factor, h is the Planck's constant, N is Avogadro's number and R is the universal gas constant. A plots of log Rate vs. 1/T and log (rate/

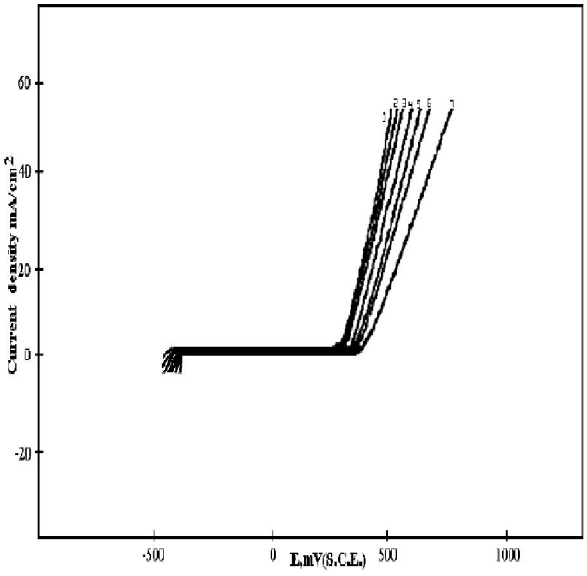


Figure 7 : Potentiodynamic anodic Polarization curves of 304 SS in 3.5 % NaCl containing different concentrations of compound (I)

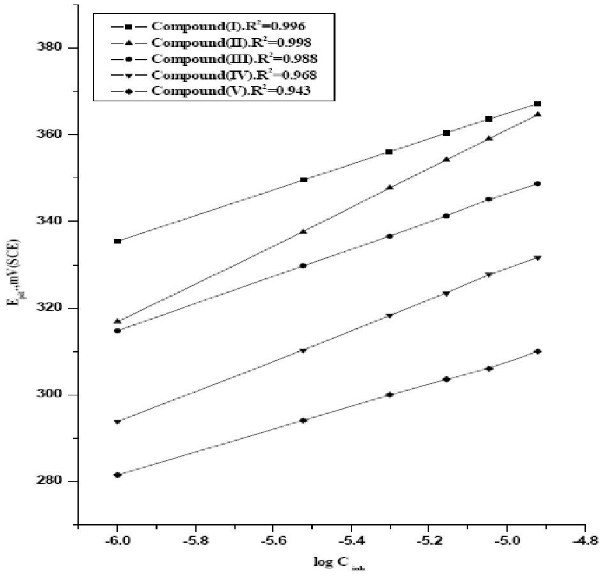


Figure 8 : The relationship between pitting potential of 304 SS and logarithm the concentration of the additives in presence of 3.5 % NaCl

T) vs. 1/T give straight lines with slope of -E_a^*/2.303R and - ΔH*/2.303R respectively. The intercepts will be A and log R/Nh + ΔS*/2.303R for Arrhenius and transition state equations, respectively.

Figure 4 represents plots of the log rate vs. 1/T and figure 5 represent log (rate/T) vs. 1/T data. The calculated values of the apparent activation energy, E_a^*, activation entropies, ΔS*and activation enthalpies, ΔH* are given in TABLE 5.

The almost similar values of E_a^* in the presence and the absence of inhibitors suggested that the inhibitors are similar in their mechanism of action and the order of efficiency may be related to the preexponential factor A in eq. (7). This is further related to concentration, steric effects and metal surface characters. According to Oguzie[33] and Abd El-Rehim[34] unchanged or lowered activation energy in inhibited system compared to blank is indicative of chemisorptions possibly, because some energy is used up in chemical reaction. The endothermic one (ΔH* > 0) is attributed unequivocally to chemisorptions, an exothermic adsorption process (ΔH*< 0) may involve either physisorption or chemisorptions or a mixture of both processes. In the present work, the positive value obtained may attributed unequivocally to chemisorptions. We remark that the addition of inhibitor has very little effect on the ΔH*, which remains unaffected. The negative values of ΔS* show that the adsorption process is an ordered phenomenon. The order of the inhibition efficiencies of thiophene derivatives as gathered from the increase in E_a^* and ΔH* values and decrease in ΔS* a value is as follows: **(I)** > **(II)** > **(III)** > **(IV)** > **(V)**.

The values of E_a^* are larger than the analogous values of ΔH* indicating that the corrosion process must involve a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume. This result verified the known thermodynamic relation between E_a^* and ΔH*[35,36] which is: **$\Delta H^* = E_a^* - RT$**.

Galvanostatic polarization

Galvanostatic polarization curves of 304 SS in 3 M HCl in the absence and presence of different concentrations of compound **(I)** at 30°C is illustrated in figure 6. Similar curves were obtained for other compounds (not shown). The electrochemical parameters of compound **(I)** such as, corrosion current density ($j_{corr.}$), corrosion potential ($E_{corr.}$), Tafel slopes (β_a and β_c), calculated from Tafel plots are given in TABLE 7 as a representative one. As it can be seen, both cathodic and anodic reactions of SS electrode were inhibited with the increase in inhibitor concentration in 3 M HCl acid. The addition of inhibitors decreases the j_{corr} values significantly for all the studied concentrations due to the increase in blocked fraction of the electrode surface by

TABLE 7 : Corrosion parameters obtain from galvanostatic polarization of 304 SS in 3M HCl containing various concentrations of inhibitor (I) at 30°C

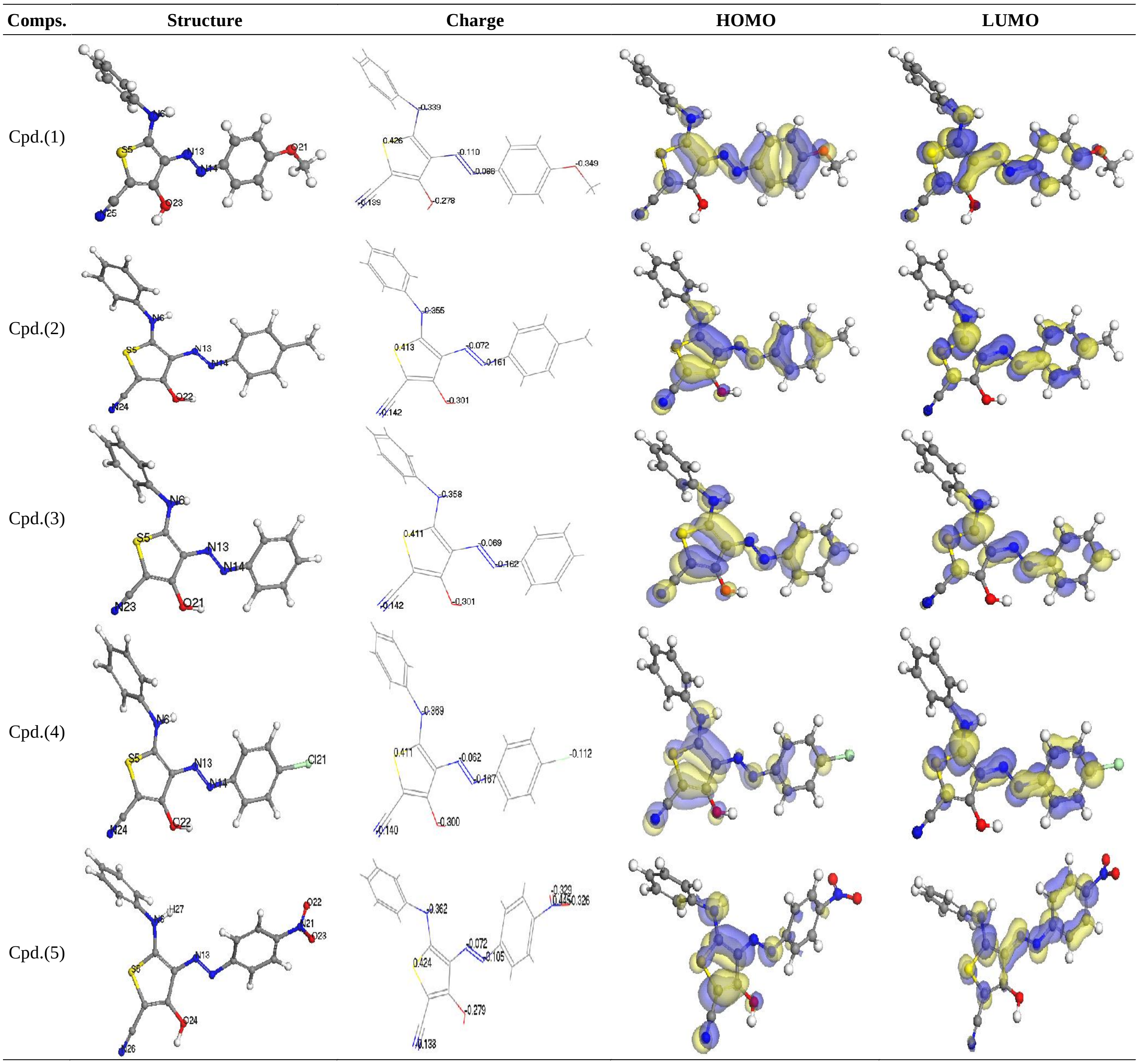
Conc. M	E_{corr} (mV vs SCE)	j_{corr}, (mA cm^{-2})	β_a (mV dec^{-1})	β_c (mV dec^{-1})	θ	IE %
0.0	331	338.78	57	73	-	-
1×10^{-6}	328	154.17	53	60	0.545	54.5
3×10^{-6}	323	144.88	50	75	0.572	57.2
5×10^{-6}	323	109.40	48	69	0.677	67.7
7×10^{-6}	324	95.72	52	71	0.718	71.8
9×10^{-6}	323	72.61	49	71	0.786	78.6
1.2×10^{-5}	321	61.94	48	73	0.817	81.7

TABLE 8 : Molecular properties of the investigated derivatives calculated with semiempirical method in aqueous phase

Compounds	$-E_{HOMO}$, (eV)	$-E_{LUMO}$, (eV)	ΔE, (eV)	η = ΔE/2, (eV)
(I)	8.56	1.00	7.56	3.780
(II)	8.79	1.10	7.69	3.845
(III)	8.80	1.10	7.70	3.850
(IV)	8.90	1.19	7.71	3.855
(V)	9.16	1.29	7.85	3.925

adsorption. It is also evident from this study that the inhibition of the SS corrosion is under both cathodic

Figure 9 : Molecular orbital plots as well as active sites for electrophilic, nucleophilic and radial attack on arylazodyes derivatives



and anodic control and these compounds do not cause significant shift in E_{corr} values, therefore these investigated compounds can be classified as mixed-type inhibitors in 3 M HCl.

It is apparent from the results that the IE % of these additives is in the order: **(I)** > **(II)** > **(III)** > **(IV)** > **(V)**.

Effect of some thiophene derivatives on the potentiodynamic anodic polarization curves of 304 SS.

The primary step in the action of corrosion inhibitors in acid solution usually adsorption of inhibitors on the metal[37]. The plots of figure 8 represent the potentiodynamic anodic polarization curves of SS type 304 electrode in 3.5% NaCl (similar to sea water) solution at a scanning rate 1 mV/sec. It was found that the pitting potential of the stainless steel electrode is shifted to more positive (noble) values with increasing the concentration of additives values this indicates that increased resistance to pitting attack in accordance with the following equation:

$$E_{pitt.} = a_2 + b_2 \log C_{inh.} \qquad (12)$$

where a_2 and b_2 are constants which depend on both the composition of additives and the nature of the electrode.

Figure 9 represents the relationship between pitting potential and the logarithmic of the molar concentration of the added compounds. Straight lines were obtained. Inhibition afforded by these compounds using the same different concentrations of the additives decreases in the following order: **(I)** > **(II)** > **(III)** > **(IV)** > **(V)**.

The inhibition efficiency depends on many factors including adsorption centers, mode of interaction, molecular size and structure[38-40]. The effect of molecular structure, size and functional group can be easily viewed from the difference in the structure of investigated thiophene derivatives.

These thiophene derivatives in the present study contain N, S, and O atoms which are in the protonated form and hence it is quickly adsorbed on the metal surface and thus forming an insoluble stable film on the mild steel surface. This is usually observed by the decrease in corrosion loss which depends on the concentration of inhibitor. The adsorption of these inhibitors onto the metals has been described in terms of concepts of “hard-soft acid and bases” and electrosorption valency. Inhibitive efficiencies change with the nature of substituent in the inhibitor molecules as electron densities change at functional groups. Substituent increase the inhibitive efficiency probably because of strong adsorption forces arising from increased electron density due to nucleophilic or electrophilic substituent. The protective efficiency is also related with steric factor.

The difference in inhibition efficiency from two methods may be attributed to the different surface status of the electrode in two measurements. In polarization measurements the electrode potential was polarized to high overpotentials, non-uniform current distributions, resulted from cell geometry, solution conductivity, counter and reference electrodes placement etc, will lead to difference between the electrode area actually undergoing polarization and total area[41].

Theoretical studies

The reactive ability of the inhibitor is related to the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital (LUMO), according to Fukui’s frontier molecular orbital theory[42]. Higher E_{HOMO} of the adsorbent leads to higher donating electron ability[43]. Low E_{LUMO} indicates that the acceptor accepts electrons easily. The calculated quantum chemical indices of investigated compounds are shown in TABLE 8. The difference $\Delta E = E_{LUMO} - E_{HOMO}$ is the energy required to move an electron from HOMO to LUMO. A low ΔE facilitates adsorption of the molecule[44] and thus will cause higher inhibition efficiency. The band gap energy ΔE increases according to: **(I)** < **(II)** < **(III)** < **(IV)** < **(V)**. This fact explains the decreasing inhibition efficiency in this order as shown in TABLE 8.

The HOMO, LUMO and electronic charge density distributions of the molecules were plotted in figure 8a and 8b, respectively. It can observe that the benzene ring attached to NH group of the thiophene ring and the thiophene ring have a large electron density.

CONCLUSIONS

(1) The investigated thiophene derivatives inhibit the corrosion of 304 SS in 3M HCl solution by being adsorbed on the metal surface and the adsorption of these inhibitors obeys Temkin’s adsorption isotherm.

(2) Galvanostatic polarization technique reveals that these thiophene derivatives are mixed-type inhibitors for corrosion of 304 SS in acidic media.

(3) The inhibition efficiency increases with increasing the inhibitor concentration but decreases with the increase of the temperature.

(4) The kinetic parameters values obtained from this study (E_a, ΔH^* and ΔS^*) indicate that the presence of thiophene derivatives decreases the E_a and the negative values of ΔG^o_{ads} indicate the spontaneous adsorption of inhibitors on the SS surface.

(5) The data obtained from the three methods namely, weight loss, galvanostatic polarization and potentiodynamic anodic polarization are in good agreement.

(6) The inhibition of these investigated compounds is governed by physisorption mechanism.

(7) Quantum chemical calculations give a correlation between parameters related to electronic structure of investigated compounds and their ability to inhibit the corrosion process. The calculated indices show good correlation with the inhibition efficiency.

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