SOME THIAZOLODINE-5-ONE DERIVATIVES AS INHIBITORS FOR THE CORROSION OF CARBON STEEL IN 2M HCl SOLUTION

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ABSTRACT

The inhibitory action of five thiazolodine-5-one derivatives on the corrosion of carbon steel in 2 M HCl at different concentrations has been investigated at $25^{\circ}C$. Weight loss, galvanostatic polarization and electrochemical impedance spectroscopy (EIS) methods, showed that the order of decreasing inhibition efficiency is: (D) > (C) > (B) > (A). Polarization method showed that these compounds act as mixed-type inhibitors. Adsorption of these compounds on carbon steel surface in 2 M HCl followed Langmuir isotherm model. A physical adsorption phenomenon is proposed. Addition of I⁻ ions to the solution containing thiazolodin-5-One derivatives increases the inhibition efficiency of the system by synergistic effect. Electrochemical impedance spectroscopy also suggests the formation of a protective layer on the steel surface by the adsorption of inhibitor molecules and chloride ions.

1. INTRODUCTION

Carbon steel is the widely used materials in the construction phases especially in the most economic projects in various aggressive environments such as chemical plants, destination plants, waste water treatment plants and petroleum industry **[Bentiss et al. (2000)]**. Organic

compounds containing polar groups including nitrogen, sulfur, and oxygen, and heterocyclic compounds with polar functional groups and/or conjugated double bonds [**Huynh et al. (2002); Khittov et al. (1964); Levin & Solomon (1963); Popva et al. (2003); al-Neani et al. (1995) and Abde Aal & Morad (2001)**] have been reported to inhibit steel corrosion. Inhibition by these organic compounds is usually attributed to their interaction with the metal surface via adsorption, either physiosorption or chemisorption involving coordinates bond formation [**Suroor et al. (2001)**]. Piperazine derivatives used as corrosion inhibitors for carbon steel corrosion [**Babic-Samardzija et al. (2005); Babic-Samardzija et al. (2005) and Bereket et al. (2003)**].

The inhibition mechanism of these organic compounds is mainly based on adsorption [**El-Kanonni et al. (1996)**]. These compounds can adsorb on the steel surface blocking the active sites and thereby decreasing the corrosion rate. They control corrosion acting over the anodic or the cathodic surface or both.
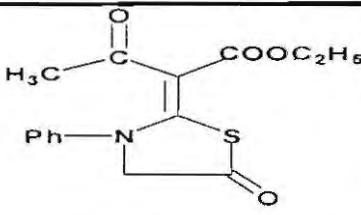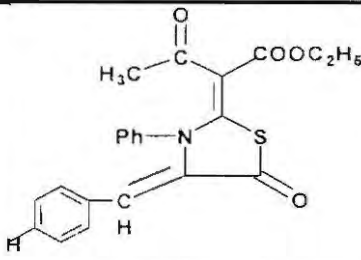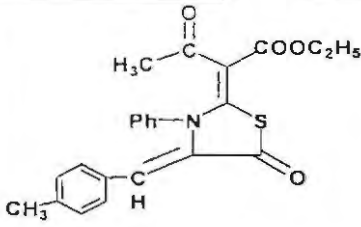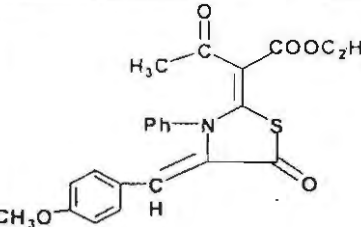
The presents work is aimed to investigate the inhibition efficiency of some **thiazolodine-5-one** derivatives on the corrosion of carbon steel in 2 M HCl solutions using weight loss, galvanostatic polarization and ac impedance measurements. The effect of temperature on the dissolution of carbon steel in free and inhibited acid solution was also, investigated.

2. EXPERIMENTAL

2.1. Materials

Carbon steel sheet composed of (weight %): C 0.2. Mn 0.35, P 0.024, Si 0.003 and the remainder iron, was used as the working electrode for all studies. Inhibitors were synthesized as highly pure grade as before [**Metwally et al. (2003)**]. Acid solutions were prepared from AR grade HCl in an appropriate concentration using double-distilled water. The exact concentration was determined using standard $NaCO_3$. KI with AR grade was used. Fig. 1 shows the molecular structures of the investigated compounds

Fig.1 Molecular structures of thiazolodine-5-One derivatives

Compound	Thiazoldine-5-one derivatives	Structural formula	Molecular weight
A	$C_{15}H_{15}NO_4S$ (Z)-ethyl 3-oxo-2-(5-oxo-3-phenylthiazolidin 2-ylidene) butanoate	COMPOUND(A)	305.10
B	$C_{22}H_{..}NO_4S$ (2Z)-ethyl 2-((Z)-4-benzylidene-5-oxo-3-phenylthiazolidin-2-ylidene)-3-oxobutanoate	COMPOUND (B)	407.15
C	$C_{23}H_{21}NO_4S$ (2Z)-ethyl 2-((Z)-4-(4-methlybenzylidene)-5-oxo-3 phenylthiazolidin-2-ylidene)-3-oxobutanoate	COMPOUND (C)	407.15
D	$C_{23}H_{21}NO_5S$ (2Z)-ethyl 2-((Z)-4-(4-methoxybenzylidene)-5-oxo-3-phenylthiazolidin-2-ylidene)-3-oxobutanoate	COMPOUND (D)	423

2.2. Chemical measurements (weight loss method)

The reaction basin 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 2×2×0.2 cm. They were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), rinsed with double 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. Triplicate experiments were performed in each case and the mean value of the weight loss is reported. The weight loss was recorded to the nearest 0.0001g. Inhibition efficiency IE % was calculated from the following equation:

$$IE\% = [(W_{corr} - W'_{corr}) / W_{corr}] \times 100 \tag{1}$$

$$\theta = [(W_{corr} - W'_{corr}) / W_{corr}] \tag{2}$$

where, W_{corr} and W'_{corr} are the weight losses of carbon steel in the absence and presence of inhibitors, respectively.

2.3. Electrochemical measurements

Electrochemical experiments were carried out in a glass cell with capacity of 100 ml. A platinum electrode and a saturated calomel electrode (SCE) were used as a counter and reference electrodes, respectively. The used strip coupons (1 cm^2) were welded from one side to a carbon steel rod for electric connection purpose and embedded in glass tube of larger diameter than the sample. Epoxy resin was used to stick the sample to the glass tube except the exposed tested surface area which was left to be exposed to the corrosive media. Prior of each experiment the working electrode was polished successively with different grades of emery paper up to 1,000, rinsed with double-distilled water, degreased by acetone, washed thoroughly with double-distilled water and dried at room temperature. The galvanostatic polarization was conducted in a PGZ301 potentiostat. A personal computer was used to collect and treat data with Volta Master 4 and Zview softwares.

The ac impedance measurements were performed at corrosion potentials after 1 h exposure of the working electrode in the solution, over a frequency range 10 mHz to 100 k Hz with a signal amplitude perturbation of 5 mV. Nyquist plots were obtained. EIS measurements

were conducted using EG&G Princeton potentiostat with software M 398. All experiments were carried out in freshly prepared solutions at constant temperature $30\pm1°C$ using thermostat. The measurements were repeated to test the reproducibility of the results. The inhibition efficiency IE % was calculated as follows:

For galvanostatic polarization measurements:

$$IE \% = [(I_{corr} - I'_{corr}) / I_{corr}] \times 100 \tag{3}$$

$$\theta = [(I_{corr} - I'_{corr}) / I_{corr}] \tag{4}$$

where. I_{corr} and I'_{corr} are corrosion current densities without and with the inhibitor. respectively and θ is the surface coverage.

For impedance measurements:

$$IE \% = [(R'_{ct} - R_{ct}) / R'_{ct}] \times 100 \tag{5}$$

where R_{ct} and R'_{ct} are charge transfer resistances without and with the inhibitor. respectively.

3. RESULTS AND DISCUSSION

3.1-Weight loss measurements

Figure (2) shows the weight loss-time curves for inhibitor (D). the most effective one. Similar curves were obtained for other inhibitors (not shown). The curves obtained in the presence of inhibitors fall significantly below that of free acid. In all cases. the increase in the inhibitor concentration was accompanied by a decrease in weight-loss and an increase in the percentage inhibition. These results lead to the conclusion that. these derivatives are fairly efficient as inhibitors for carbon steel dissolution in HCl solution. Also. the degree of surface coverage, (θ) would increase by increasing the inhibitor concentration.

In order to get a comparative view, the variation of the inhibition efficiencies (IE %) of the inhibitors with their molar concentrations were calculated according to equation (1) and recorded in Table 1. Careful inspection of these results showed that at the same inhibitor concentration, the order of inhibition efficiency is decrease as follows:

(D) > (C) > (B) > (A).
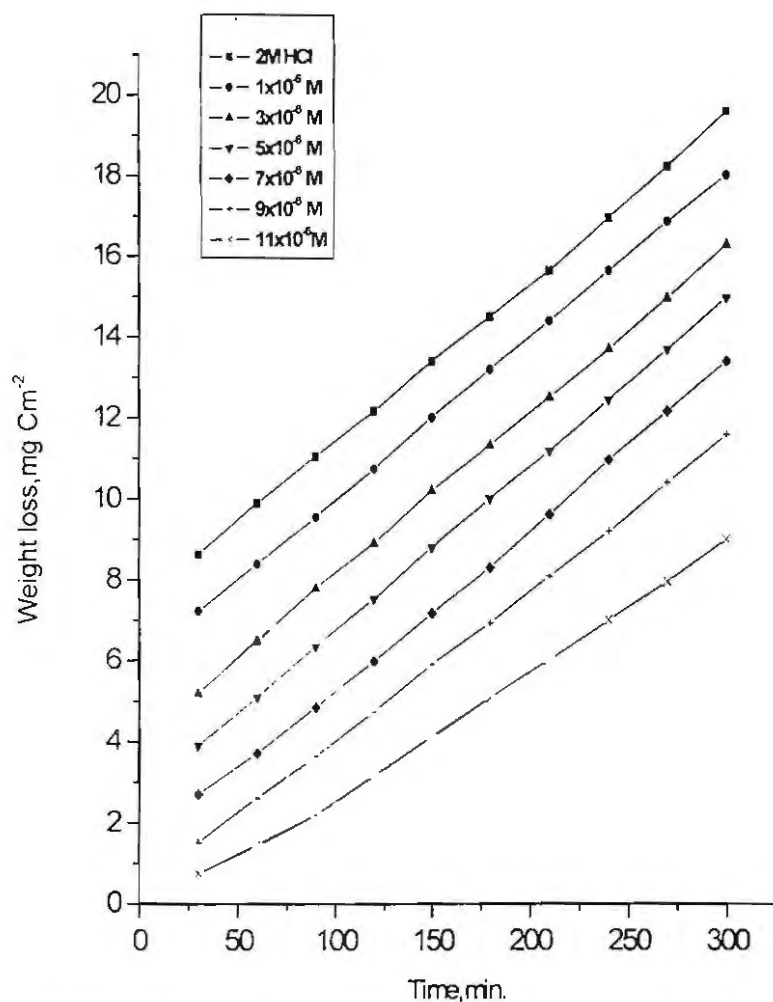
Fig.(2) Weight loss-time curves for C-steel in the presence and absence
of different concentrations of compound (D) at 30^0 C

3.2. Synergistic effect

As shown from Table (1), the % inhibition efficiency of the tested derivatives is moderate, consequently, in order to increase these values we use KI in addition to the different concentrations of the investigated derivatives. Table (2) shows the % inhibition of the investigated derivatives in presence of 1×10^{-2}M of KI.

Table (1): % Inhibition of carbon steel dissolution at 210 min. immersion in 2 M HCl in presence of different concentrations of inhibitors at 30°C.

Concentration, M	IE %			
	(A)	(B)	(C)	(D)
1×10^{-6}	12.5	12.9	13.4	18.0
3×10^{-6}	18.0	19.6	20.8	20. 9
5×10^{-6}	25.3	26.4	28.3	28.5
7×10^{-6}	46.3	47.1	38.2	38.5
9×10^{-6}	42.9	42.3	43.6	48.3
11×10^{-6}	62.6	63.7	70.4	71.6

Table(2): %Inhibition efficiency of carbon steel dissolution at 210 min. immersion in 2M HCl in presence of 1×10^{-2}M KI at different concentrations of inhibitors at 30°C.

Concentration, M	IE %			
	(A)	(B)	(C)	(D)
1×10^{-6}	13.0	16.2	18.2	21.4
3×10^{-6}	17.3	18.0	19.8	35.8
5×10^{-6}	28.2	37.5	37.9	43.9
7×10^{-6}	32.5	42.1	43.1	49.5
9×10^{-6}	41.2	60.4	61.5	75.5
11×10^{-6}	46.8	70.0	77.6	79.5

It can be seen from Table (2) that the addition 10^{-2} M of KI inhibits the corrosion of carbon steel to a large extent and by increasing the concentration of thiazolodine-5-one derivatives (1×10^{-6}- 11×10^{-6} M). This can be interpreted according to Schmitt and Bedbur **[Schmilt & Bedbur (1985)]**, which proposed two types of joint adsorption namely competitive and cooperative. In competitive adsorption, the anions and cations are adsorbed at different sites on the electrode surface, and in case of cooperative adsorption, the anions are chemisorbed on the electrode surface and the cations are adsorbed on a layer of the anion, apart from the adsorption on the surface directly. However, the addition of KI to the above system resulted in significant decrease in corrosion rate. It is clear that I⁻ anions play a dominate role in the corrosion inhibition of steel in the presence of these inhibitors. The inherent reason

is that the steel surface has positive charge and it is difficult for the positively charged inhibitor molecules to approach this positively charged steel surface. However, the specific adsorption of I^- on the positively charged steel surface by means of electrostatic attraction results in a negatively charged surface layer. Thus cationic inhibitor molecules can be adsorbed readily on the steel surface by electrostatic interaction between I^- layer and the cationic inhibitor, thus leading to a significant decrease in corrosion rate. The synergistic effect depends on the type and concentration of anions. Also, the presence of this anion in the solution stabilizes the adsorption of derivatives on the metal surface and improved the inhibition efficiency of these derivatives.

Fig. (3) Demonstrates the weight loss time curves for the dissolution of C-Steel in 2 M HCl in the absence and presence of different concentrations of compound (D) without and with addition of 10^{-2} M KI at 30°C.

3.3. The adsorption isotherm

Assuming that corrosion inhibition was due to the adsorption of thiazolodine-5-one derivatives, the degree of surface coverage, θ, was calculated from weight loss method using equation (2).

Adsorption of organic adsorbate at the metal/solution interface can be represented by a substitutional adsorption process between organic molecules in the aqueous solution $Org_{(sol)}$ and water molecules on the metallic surface $Org_{(sol)}$ [**Bockris & Swinkels (1964)**].

$$Org_{(sol)} + x\ H_2O_{(ads)} = Org_{(ads)} + xH_2O_{(sol)} \tag{6}$$
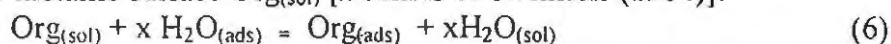
where $Org_{(sol)}$ and $Org_{(sol)}$ are the organic molecules in the aqueous solution and those adsorbed on the metallic surface, respectively, $H_2O_{(ads)}$ are water molecules on metallic surface, x is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate.

The inhibition mechanism can be explained as before [**Bockris & Drazic (1962)**]:
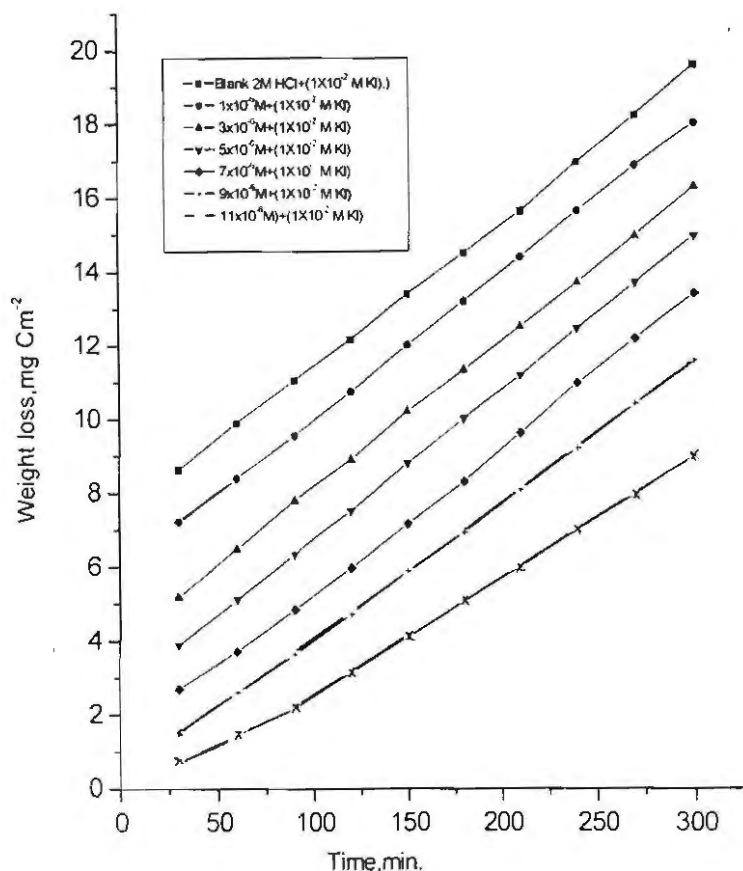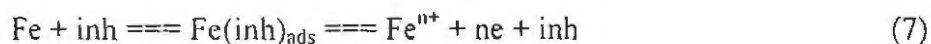
Fig.(3) Weight loss-time curves for C-steel in presence of 1×10^{-2}M KI
with different concentrations of compound (D) at 30^0 C

$$Fe + inh === Fe(inh)_{ads} === Fe^{n+} + ne + inh \qquad (7)$$

Initially, the metal dissolution takes place on sites of the steel surface free from Fe $(inh)_{ads}$, because: i) insufficient inhibitor's concentration or ii) the slow rate of the adsorption. But if the inhibitor concentration is high enough, a coherent layer will be formed on the steel surface, reducing chemical attack of the metal [Branzoi et al. (2000)].

When equilibrium is reached in equation (7), it becomes possible to obtain different expressions for the adsorption isotherm plots.
Data of θ were found to fit with the Langmuir isotherm, given by:

$$(C/\theta) = 1/K + C \tag{8}$$

$$\text{With } K = 1/55.5 \exp(-\Delta G^{o}_{ads}/RT) \tag{9}$$

C is the concentration of the inhibitor in the bulk solution, K the adsorption equilibrium constant and ΔG^{o}_{ads} the free energy of adsorption. Fig.4 shows the plot of C/θ vs. C, this plot gives straight lines with slopes very close to 1, which confirm the Langmuir adsorption isotherm mechanism. This means that there is no interaction among the adsorbed species [El-Etre (2001)]. A linear regression calculated for these lines is more than 0.99. On the other hand, it is found that kinetic-thermodynamic model of El-Awady et al [El-Awady & Ahmed (1985)] which has the formula:

$$\log(\theta/1-\theta) = \log K^{*} - y \log C \tag{10}$$

Is valid and verify the present adsorption data (Fig.5). The equilibrium constant of adsorption $K = K^{*(1/y)}$, where 1/y is the number of the surface active sites occupied by one thiazolodine-5-one molecule and C is the bulk concentration of the inhibitor. From Table (3) it is noted that ΔG^{o}_{ads} values have a negative sign indicating that the adsorption process proceeds spontaneously and increase as the percentage inhibition increases. Table (3) shows the calculated thermodynamic parameters.
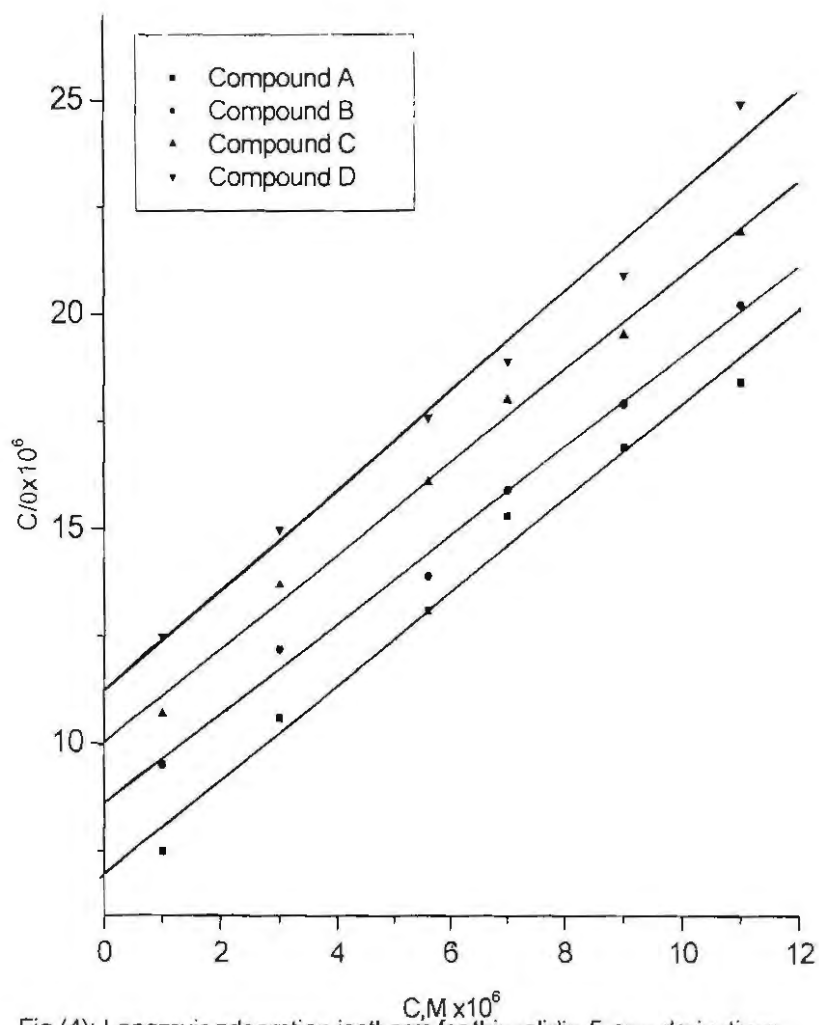
Fig.(4): Langmuir adsorption isotherm for thiazolidin-5-one derivatives on C-Steel in 2M HCl at 30°C.
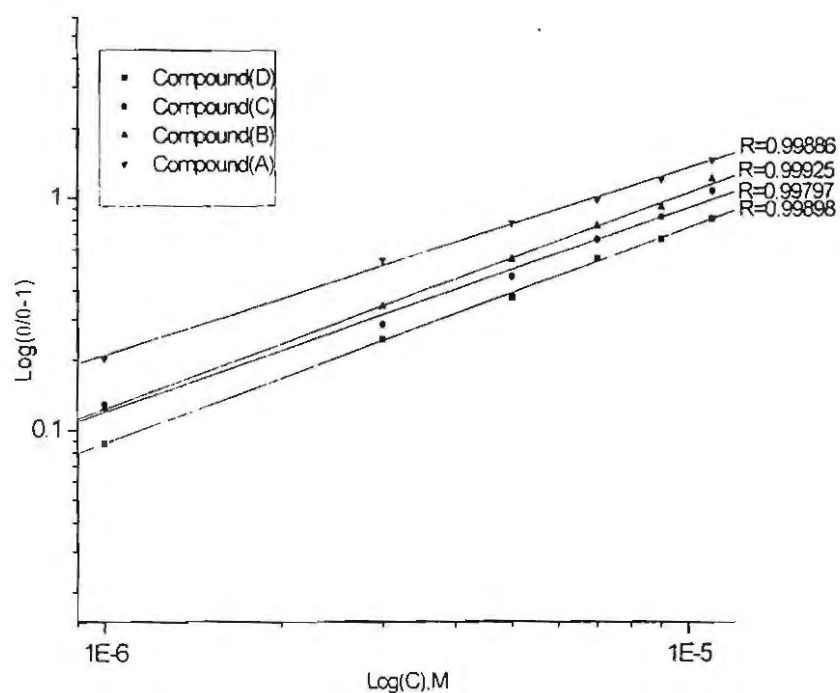
Fig.(5.): Curve fitting of corrosion data for C-steel in 2M HCl in presence of different concentrations of inhibitors to the kinetic model at 30°C

Table (3): Inhibitor binding constant (K), free energy of binding ($\Delta G_{ads.}$), number of active sites (1/y) and later interaction parameter (a) for thiazolidine derivatives at 30°C.

Inhibitors	Kinetic model			Langmuir Isotherm		
	1/y	$K \times 10^{-4}$	$-\Delta G_{ads}$, kJmol^{-1}	a	$K \times 10^{-4}$	ΔG_{ads}, kJmol$^-$
(A)	0.24	1.6	11.2	1.09	14.1	40.1
(B)	0.21	1.6	11.3	1.05	11.5	39.5
(C)	0.23	1.6	11.4	1.11	10.1	39.1
(D)	0.22	1.6	11.8	1.16	8.8	38.8

3.4. Effect of Temperature

The effect of temperature (30 – 50°C) on the corrosion behavior of C-steel in the presence and absence of thiazolodine-5-one derivatives at concentrations of (1×10^{-6} - 11×10^{-6} M) in 2M HCl was studied using weight-loss method. The inhibition efficiency of inhibitors deceases with temperature. The activation energies for the correction process were calculated from the Arrhenius equation:

$$k = A \exp(-E_a^* / RT) \tag{11}$$

where E_a^* represents the apparent activation energy the gas constant, T the absolute temperature, A the pre-exponential factor and k the corrosion rate.

Arrhenius plots for the corrosion rate of C-steel are given in (Fig.6). Values of E_a^* for C-steel in 2 M HCl in the absence and presence of various concentrations of inhibitors were determined from the slopes of ln k vs. 1/T plots.

The values of E_a^* in the absence of inhibitors (37.8 kJ mol^{-1}) in 2M HCl agrees well with literature data of E_a^* for iron and C-steel in HCl. which are in the range 38-48 kJ mol^{-1}. In the presence of inhibitors E_a^* are (38.9 – 43.5) kJ mol^{-1}.

It is clear that the presence of inhibitors increases the activation energies of C-steel than in absence indicating the presence of these inhibitors induces energy barrier for the corrosion reaction and this barrier increases with increasing the inhibitor concentrations. Chemisorption of the inhibitors associated with an increase in activation energy but physisorption associated with decrease in activation energy, this as reported before [**Abdel-Rahim et al. (2002); Barcia et al. (1993) and Deslouis et al. (1988)**]. So. we can conclude that these inhibitors exert their effects through physisorption on the surface. It retards the corrosion at lower temperature but its inhibition effect diminishes at elevated temperatures.

The enthalpy and entropy of activation cab be calculated from transition state- type equation:

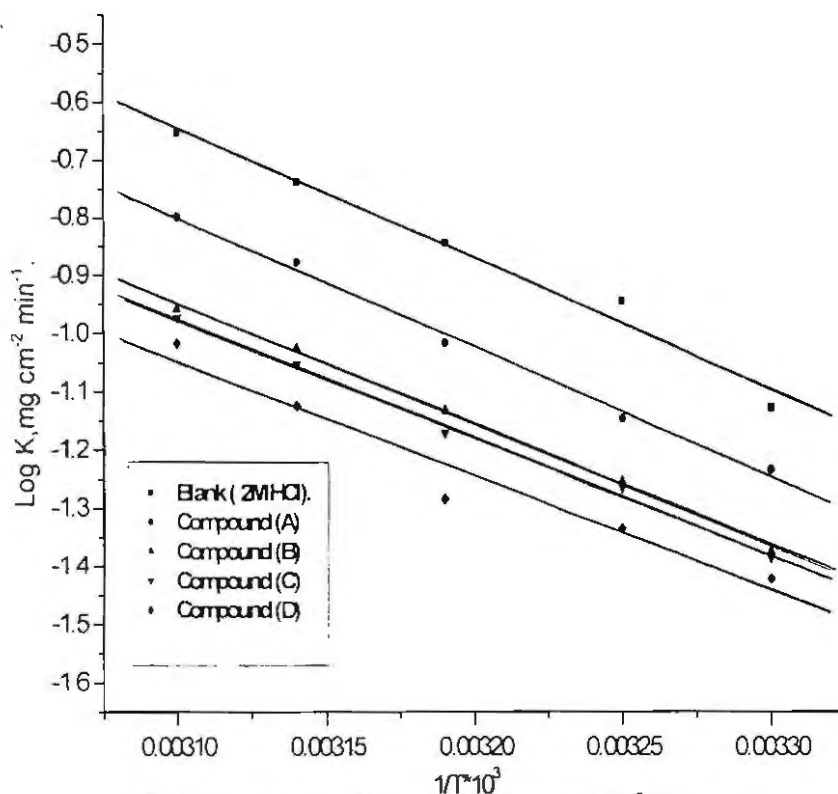$$k = RT / Nh \exp(\Delta S^*/R) \exp(-\Delta H^* / RT) \tag{12}$$

Fig (6): Log corrosion rate vs. 1/T for C-Steel in presence of 5x10^{-6}M of thiazolidine Derivatives compounds at 210 min immersion

The relation between log k/T vs. 1/T gives straight lines (Fig.7), from their slopes, ΔH^* can be calculated and from their intercepts ΔS^* can be also calculated. Table (4) exhibits the values of apparent activation energy E_a^*, enthalpies ΔH^* and entropies ΔS^* for C-steel dissolution in 2M HCl solution. The decrease in the activation enthalpy (ΔH^*) in presence of the inhibitors implies that the addition of the inhibitors to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the present inhibitor. The entropy of activation (ΔS^*) in the blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step.
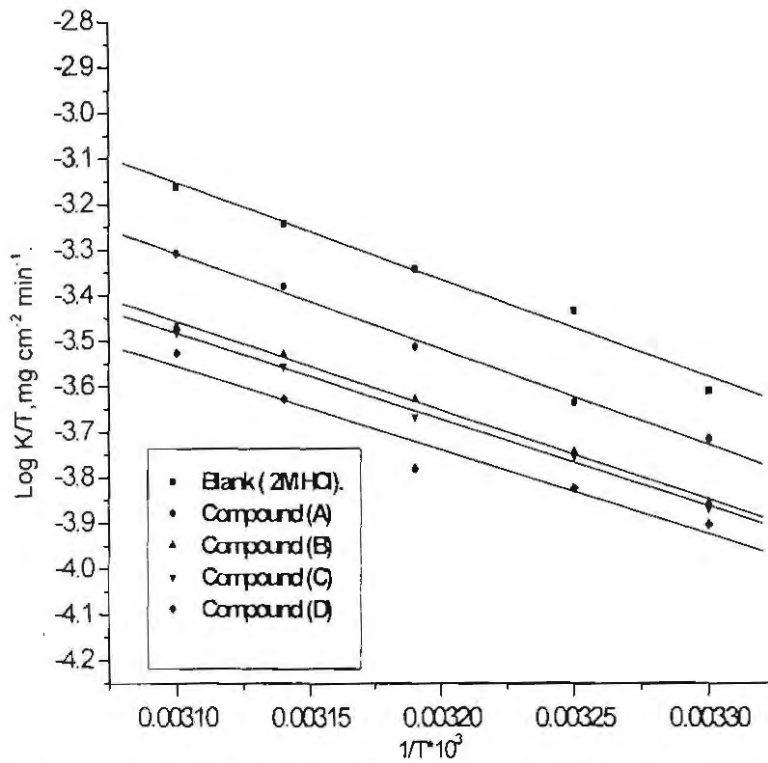
Fig.(7): Log corrosion rate/T vs. 1/T for C-Steel in presence of 5x10⁻⁶M of thiazolidine derivatives at 210 min immersion

Table (4): Effect of concentrations of inhibitors on the activation energy, activation enthalpy and activation entropy of C-STEEL dissolution in 2M HCl.

Inhibitor	Concentration, M	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, K^{-1}J mol^{-1}
Blank	0.0	37.8	49.3	130.8
A	5X10⁻⁶M	38.9	40.3	135.8
B	5X10⁻⁶M	40.0	37.4	147.6
C	5X10⁻⁶M	42.9	36.4	151.3
D	5X10⁻⁶M	43.5	35.2	156.3

3.5 Electrochemical methods
3.5.1. Polarization studies

Corrosion behavior of carbon steel is studied in 2M HCl solution in the absence and presence of $(1\times10^{-6} - 11\times10^{-6}M)$ inhibitors (A –D) at 30°C. Fig. (7) shows the anodic and cathodic curves of C- steel in 2M HCl in the absence and presence of different concentrations of inhibitor (D). Similar curves were obtained for other inhibitors (not shown). Table (5) gives the values of Tafel slopes (β_a & β_c), corrosion potential (E_{corr}), corrosion current (i_{corr}), degree of surface coverage (θ) and inhibition efficiency (P %). The presence of inhibitors causes a marked decrease in corrosion rate, i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be ascribed to adsorption of inhibitor over the surface. From Table 5, it can see that the corrosion current density decreases with increasing the concentration of thiazolidine -5-One derivatives. This indicates that the presence of these derivatives retards the dissolution of C- steel in 2M HCl solution and the degree of inhibition depends on the concentration and type of the inhibitor present. The order of decreasing the inhibition efficiency of the thiazolidine -5-One additives is as follows: (D) > (C) > (B) > (A).

3.5.2. Electrochemical impedance spectroscopy (EIS)

EIS measurements were carried out to evaluate the data obtained from polarization and weight loss as well as the performance of thiazolidine -5-One derivatives against the corrosion of C-steel in 2 M HCl. Fig. (9) shows The Nyquist plot for C-steel in 2 M HCl with and without different concentrations of compound (D) at 30°C. The impedance diagrams show a depressed semicircle. This behavior has been described and discussed by many authors **[Abdel-Rahim et al. (2002); Barcia et al. (1993) and Deslouis et al. (1988)]**. In all cases, it is found that the diameter of the capacitive loop increases with increase in inhibitors concentrations. The change in the concentration of the thiazolidine -5-One additives did not alter the shape of the impedance behavior, suggesting that inhibition is accomplished by adsorption on electrode surface without detectable changes in the chemistry of corrosion.
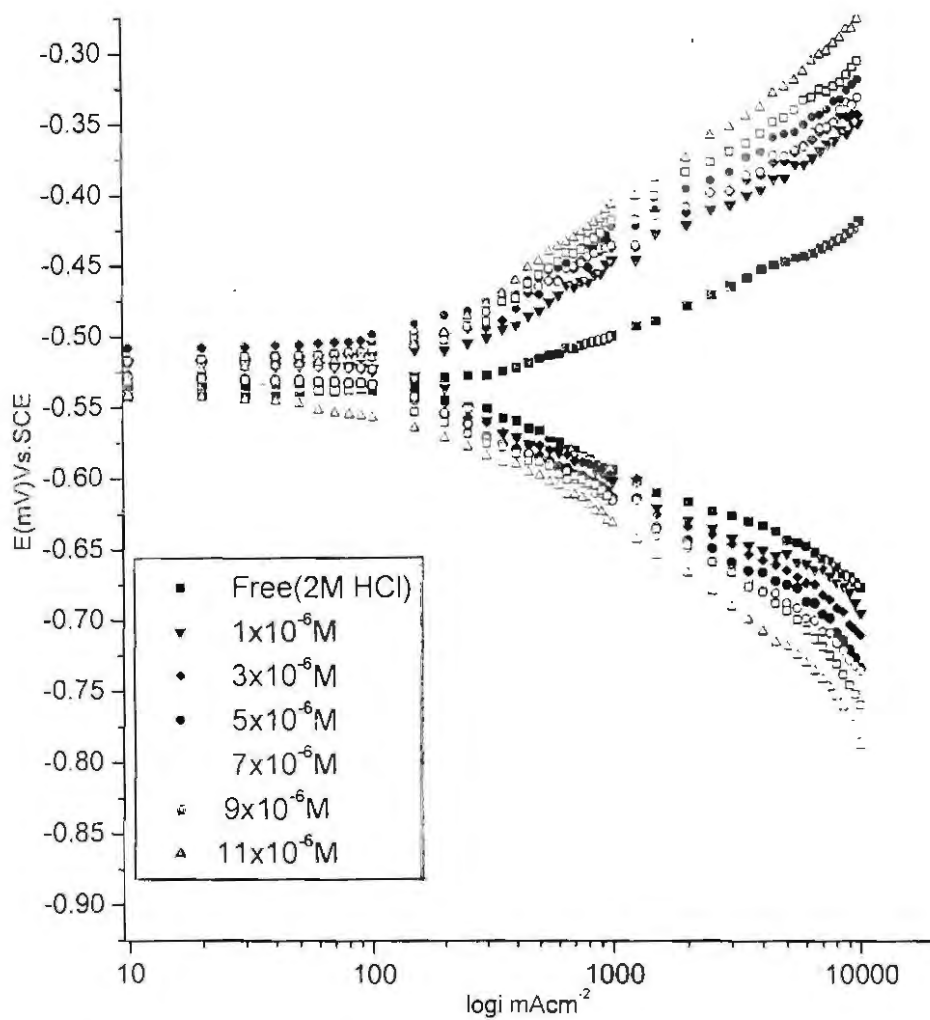
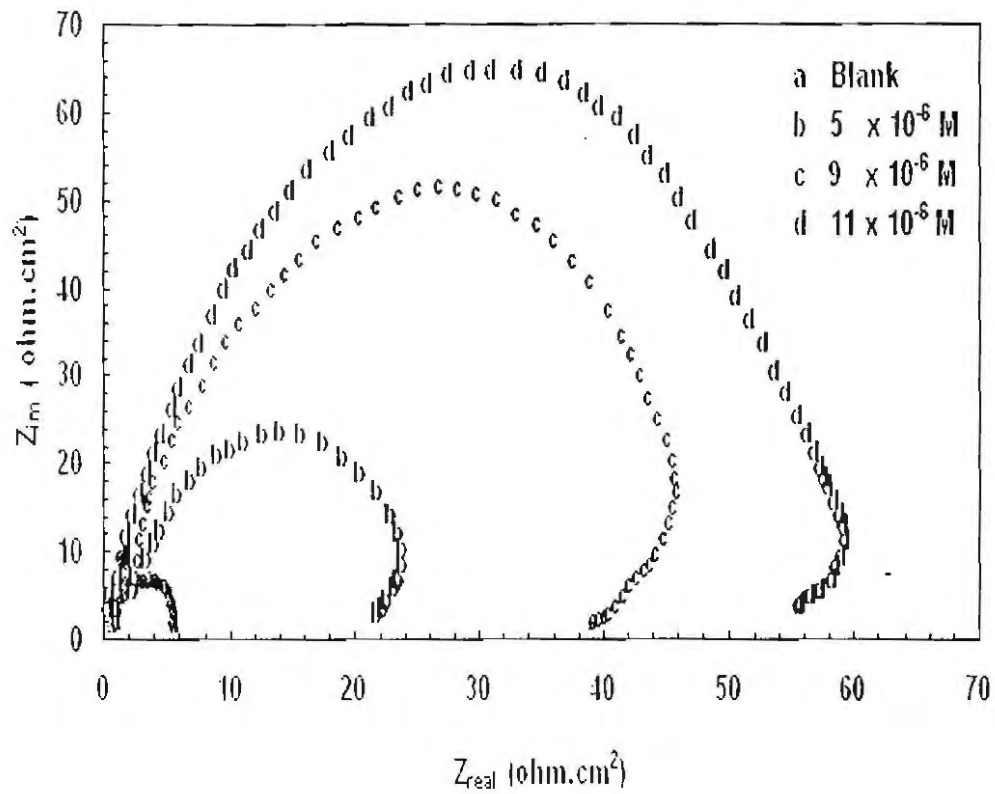Fig. (8):Polarization curves of C-steel in 2M HCl in absence and presence of different concentrations of compound (D).

Fig. (9): Nyquist plots for C-steel in 2 M HCl with and without different concentrations of compound (D) at 30°C.

Table (5): Corrosion parameters for carbon steel in 2M HCl in the absence and presence of different concentrations of inhibitors (A-D) at 30°C.

Inhibitor	Conc., M	$-E_{corr}$, mV	i_{corr}, μAcm^{-2}	β_a, mVdec^{-1}	β_c, mVdec^{-1}	θ	IE %
Blank	2M HCl	537	227.9	72	73	–	–
A	1×10^{-6}	532	144.5	73	95	0.240	24.0
	3×10^{-6}	530	117.5	85	98	0.382	38.2
	5×10^{-6}	528	84.9	87	100	0.553	55.3
	7×10^{-6}	525	75.0	·100	103	0.606	60.6
	9×10^{-6}	512	68.0	108	106	0.642	64.2
	11×10^{-6}	508	217.6	114	109	0.748	74.8
B	1×10^{-6}	534	217.6	73	75	0.211	21.1
	3×10^{-6}	530	207.8	86	91	0.371	37.1
	5×10^{-6}	523	195.0	95	97	0.530	53.0
	7×10^{-6}	520	184.6	105	100	0.631	63.1
	9×10^{-6}	515	174.5	109	105	0.708	70.8
	11×10^{-6}	505	151.2	122	110	0.829	82.9
C	1×10^{-6}	535	219.2	79	75	0.182	18.2
	3×10^{-6}	525	210.6	80	79	0.329	32.9
	5×10^{-6}	518	203.2	91	90	0.434	34.4
	7×10^{-6}	512	187.5	102	93	0.606	60.6
	9×10^{-6}	508	153.2	108	97	0.821	82.1
	11×10^{-6}	500	127.1	130	112	0.902	90.2
D	1×10^{-6}	530	220.2	82	78	0.163	16.3
	3×10^{-6}	525	206.0	93	82	0.396	39.6
	5×10^{-6}	520	192.4	99	84	0.558	55.8
	7×10^{-6}	515	174.3	105	90	0.709	70.9
	9×10^{-6}	512	154.1	117	100	0.817	81.7
	11×10^{-6}	510	122.5	138	117	0.912	91.2

The measured complex plane impedance plots are similar to that calculated by the equivalent circuit models [**Khaled (2003) and Khaled & Hackerman (2003)**]. In order to get more information about the corrosion inhibition phenomenon, solution resistance R_s (R_Ω), charge transfer resistance, R_{ct}, and double layer capacitance, C_{dl}, are of great

important. Impedance parameters, such as, charge transfer resistance R_{ct}, which is equivalent to R_p, and the double layer capacitance C_{dl} are derived from the Nyquist plots and are given in Table (8) for C-steel in 2M HCl solution in the presence and absence of the used thiazolidine -5-One. It is observed that the values of R_{ct} increase with increasing the concentration of the inhibitors. This due to the decrease in local dielectric constant and/or an increase in the thickness of the double layer. suggesting that these derivatives inhibit the C-steel corrosion by adsorption at the C-steel/solution interface [**Lagrence et al. (2002)**]. The thickness of this protective layer increases with increasing inhibitor concentration. This trend is in accordance with the Helmholtz model, given in equation (13):

$$C_{dl} = \varepsilon\varepsilon_0 \, A/d \qquad\qquad (13)$$

Where d is the thickness of the protective layer, ε is the dielectric constant of the medium. ε_0 is the vacuum permittivity and A is the effective surface area of the electrode. Also. the results in Table 8 show that the corrosion inhibition efficiencies for all additives obtained from EIS are in the following order: (D) > (C) > (B) > (A) and are in good agreement with those obtained from other methods.

Table (6): Data obtained from EIS measurements for C-steel in 2M HCl in presence and absence of different concentrations of all additives at 30°C.

compound	Concentration (M)	R_{CT} Ohm cm^2	C_{dl} µF cm^{-2}	θ	IE%
	0	5.3	1987.56	-	-
A	5×10^{-6}	6.2	1676.32	0.142	14.2
	9×10^{-6}	8.2	1498.5	0.351	35.1
	11×10^{-6}	10.5	1023.02	0.495	49.5
B	5×10^{-6}	7.5	1245.87	0.291	29.1
	9×10^{-6}	13.0	987.45	0.590	59.0
	11×10^{-6}	24.0	741.23	0.778	77.8
C	5×10^{-6}	10.0	875.98	0.470	47.0
	9×10^{-6}	18.5	665.23	0.714	71.4
	11×10^{-6}	36.9	254.65	0.856	85.6
D	5×10^{-6}	21.4	546.56	0.751	75.1
	9×10^{-6}	38.0	365.75	0.860	86.0
	11×10^{-6}	53.7	186.45	0.901	90.1

3.6. Quantum calculations

The results obtained from the relation between inhibition characteristics and quantum chemical data show that log $i_{corr.}$ mostly depends upon the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It is evident that the inhibition efficiency increases with the increase of energy of the HOMO, that is, the increase of the ionization potential. It is further evident that the inhibition efficiency increases with the ease of ionization of the molecule, which means that the molecule acts as an electron donor when blocking the corrosion reaction and vice versa in case of the energy of LUMO. The results of Table (7) show that the energies of HOMO orbital of the thiazolidine -5-one compounds are in the following order: D) > (C) > (B) > (A). As one can see that the inhibition efficiency of the thiazolodine-5-one derivatives calculated runs parallel to that calculated from other methods (weight loss, galvanostatic polarization, and ac impedance spectroscopy). This indicates the validity of the results and supports the discussion given for the effect of chemical composition on the inhibition action of these compounds.

Table (7): Quantum chemical parameters for 11×10^{-6}M of thiazolidine-5-one derivatives

Inhibitor	log i_{corr} $\mu A\ cm^{-2}$	-HOMO eV	-LUMO eV
Compound (A)	2.3377	9.526	0.838
Compound (B)	2.1796	9.460	0.990
Compound (C)	2.1041	9.402	1.141
Compound (D)	2.0881	9.320	1.161

Log i_{corr} = 2.3577 for 2 M HCl

3.7. Mechanism of inhibition

Inhibition of C-steel corrosion in 2M HCl solution by the investigated thiazolidine -5-one derivatives as measured by weight loss, galvanostatic polarization, and electrochemical impedance spectroscopy methods could, depend on the number of adsorption sites in the molecule

and their charge density, molecular size, and stability of these compounds in acid solutions. The order of inhibition efficiency is: (D) > (C) > (B) > (A). Compounds (D), (C) and (B) have the same structure [i.e. the centers of adsorptions (3 centers)] but the difference is the substituent group in the benzylidene ring. In compound (D) there is an –OCH$_3$ in the p-position in the benzylidene ring with σ = -0.27 (σ is the Hammett constant, a positive value of σ indicates an electron-withdrawing group and a negative value an electron-donating group), but in compound (C) there is an –CH$_3$ in the p-position in the benzylidene ring with σ =-0.17 which is less than in compound (D), so compound (D) is efficient in IE% than compound(C). Compound (B) has –H atom in the p-position in the benzylidene ring with σ = 0.00. So, compound (B) comes after compound (C) in IE%. Compound (A) is the least efficient inhibitor. This is due to its lower molecular size and lower number of adsorption centers. So the only factor which affects the adsorption of these compounds on C-steel surface is the type of the substituent group in the benzylidene ring and the molecular size of these compounds.

Skeletal representation of the mode of adsorption of the thiazolidine -5-One derivatives is shown in Figure (10) and clearly indicates the adsorption centers of these compounds on metal surfaces.
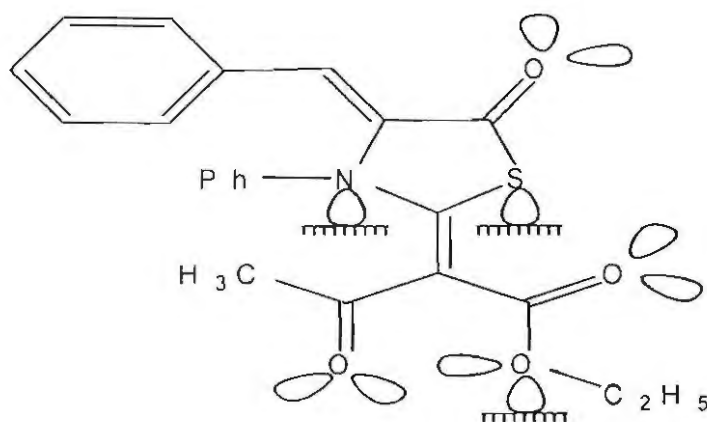

Fig.(10): Skeletal representation of the mode of adsorption of the thiazolidine -5-One derivatives (D, C, B)

4. CONCLUSIONS

The following conclusions can be deduced from the present study:

1) Thiazolodine-5-one derivatives appear to be efficient inhibitors for corrosion of C-steel in 2M HCl solution, which act as mixed-type inhibitors, the IE %was found to increase with increase the inhibitor concentration and was found that the inhibition efficiency decrease in order: (D) > (C) > (B) > (A).

2) The inhibition of corrosion of SS type 316 L in 3M HCl solution was found to obey the Langmuir adsorption isotherm and the inhibitors appear to absorb on C-Steel surface.

3) The inhibition efficiency (IE%) increases with the increase in the inhibitor concentration, while decreases with the increase in the temperature.

This means that these inhibitors adsorbed physically on C-steel surface.

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بعض مشتقات الثيازولودين كمثبطات لتأكل الصلب الكربونى فى محلول 2 مولر حامض الهيدروكلوريك

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تم دراسة التأثير المثبط لتركيزات مختلفة لخمس مشتقات من ثيازولودين –5- اون على تأكل الصلب الكربونى فى 2 مولر حمض الهيدروكلوريك عند 25° م بطرق الفقد فــى الوزن وطريقة الاستقطاب الجلفانوستاتيكى وكذلك طريقة المعاوقة الكهربائية الطيفية ودلــت النتائج على أن كفاءة تثبيط هذة المشتقاط كالتالى: $D > C > B > A$

وقد دلت طريقة الاستقطاب الجلفانوستاتيكى لهذة المركبات أنها تعمل كمثبطات مختلطة وأنها تدمص على سطح الصلب الكربونى فيزيائيا طبقا لايزوثيرم لانجمير وقد وجد ان اضافة ايون اليود فى وجود تركيزات مختلفة من هذة المشتقات يعمل على زيادة كفاءة التثبيط كما دلــت طريقة المقاومة الكهربائية على تكوين طبقة من هذة المشتقات على سطح الصلب الكربونى.