Int. J. Electrochem. Sci., 12 **(2017)** 4543 – 4562, doi: 10.20964/2017.05.35

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Corrosion Inhibition of Stainless Steel Type 316 L in 1.0 M HCl Solution Using 1,3-Thiazolidin-5-one Derivatives

M. Abdallah[1, 2, *], *M.M. Salem*[3], *B. A. AL Jahdaly*[1], *M.I. Awad*[1,4], *E. Helal*[2], *A.S. Fouda*[5]

[1] Chem. Dep., Faculty of Applied Sciences, Umm Al-Qura University, Makkah, Saudi Arabia.
[2] Chem. Dep., Faculty of Science, Benha University, Benha, Egypt
[3] Chem. Dep., Faculty of Education in Zulfi, Majmaah University, Saudi Arabia
[4] Chem. Dep., Faculty of Science, Cairo University, Cairo, Egypt
[5] Chem. Dep., Faculty of Science, El-Mansoura University, El-Mansoura, Egypt
[*]E-mail: metwally555@yahoo.com

Received: 12 December 2016 / *Accepted:* 17 February 2017 / *Published:* 12 April 2017

Ten compounds of 1,3-thiazolidin-5-one derivatives has been evaluated as an inhibitor for corrosion of stainless steel type 316L (316SS) in1.0 M HCl solution by means of weight loss and electrochemical impedance spectroscopy techniques. The surface examination and morphological studies were studied using scanning electron microscope (SEM) and energy dispersive X-ray (EDX). It has been found that the percentage inhibition efficiency increases with increasing the concentration of inhibitors and with decreasing temperature. These compounds acted as mixed type inhibitors. The inhibition process was explained due to the adsorption of these compounds at the 316 SS surface. The adsorption obeys Temkin's isotherm. The effect of substituted group and substituted position on the inhibition efficiency were explained.SEM and EDS confirmed that the rate of 316SS corrosion in1.0 M HCl solution is reduced due to the formation of the protective film on its surface.

Keywords: 316 stainless steel, 1,3-thiazolidin-5-one derivatives, corrosion inhibitors, adsorption.

1. INTRODUCTION

Stainless steel of Type 316L (316SS) used in several applications in the industry due to highly corrosion resistant. The resistance of 316 SS to corrosion attack arises from the formation of the protective film on their surface [1]. This film is corroded when subjected to acidic media especially HCl. It is possible to reduce the corrosion rate by adding inhibitors. Many organic compounds used to inhibit the corrosion of different type of stainless steel in acidic media [2-20]. The occurrence of one or more heteroatoms with high electron density, such as nitrogen, sulfur, oxygen, phosphor, or those containing multiple bonds in the chemical structure of organic compounds led to facilitate the adsorption center. Hence, the protection and the percentage inhibition efficiency of metals and alloys

increases. The results obtained from the previous studies, the hetro compounds inhibit the corrosion by its adsorption on the steel surface through hetro atoms, conjugated double bonds or aromatic rings in their molecular structure [2,13]. In addition, the adsorption of hetro compounds on the steel surface is influenced by the chemical structure of inhibitors, the nature and charged surface of metal and the type of corrosive solution.

This aim of this manuscript is to study the inhibiting effect of ten compounds of 1,3-thiazolidin-5-one derivatives toward the corrosion of stainless steel type 316L (316SS) in1. 0 M HCl solution. Some techniques are used in this study such as weight loss, electrochemical impedance spectroscopy (EIS), and surface examination (SEM and EDX). The nature of adsorption of the inhibitors at the surface and the adsorption isotherms fit the experimental results were identified

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The chemical composition of AISI 316L stainless steel (316 SS) used in the present study are: (wt.%) C 0.025, Cr 17.01, Ni 12.03, Mn 1.40, P 0.028, S 0.003, Si 0.40, Mo 2.05 and the balance is Fe

2.2. Techniques

For weight loss measurements, 316 SS coupons having dimension 1.0x 1.0 x 0.2 cm^3 were abraded with a different grades of emery papers and then washed with bi distilled water and acetone. Finally, dried between two filter papers. Complete wetting of the surface was taken as an indication of its cleanliness. The procedure methods of weight loss measurements were carried out as described elsewhere [21,22].

For electrochemical impedance spectroscopy (EIS). A cylindrical rod embedded in Araldite with an exposed surface area of 0.56 cm^2 was used. A three-compartment cell with a saturated calomel reference electrode (SCE) and a Pt foil was used as an auxiliary electrode. The pretreatment of the electrode as described previously in weight loss measurement. All chemicals used were of A.R. quality.The solutions used were freshly prepared using distilled water. The experiments were carried out at 30 ±1 ^oC using air thermostat.

The electrochemical impedance spectroscopy (EIS) measurements were performed using a Radiometer Model 40 instrument and Voltamaster 4 program as measurement software. The impedance was measured from; 10^{-3} Hz to 100 KHz, at an amplitude of 5 mV.

2.3. Surface investigation techniques:

2.3.1. Scanning Electron Microscope

JEOL Scanning Electron Microscope (SEM) model T-200, was used to examine the surface of of 316 SS immersed in the test solutions which contain 1M HCl, (1M HCl + certain concentration of each compound of 1,3-thiazolidin-5-one derivatives). The tested specimens of the 316 SS used,

samples and surface products formed during the previous studies. After the surface treatment, the specimens were stored in a desiccator until required for examination.

2.3.2. X-ray photoelectron spectroscopy:

X-ray diffraction studies were carried out on the same samples using an X-ray photoelectron spectroscopy (XPS)technique of model EDAX was used in this work. The idea of this technique depends on the ejection of electrons from the inner shells, where the energy released appears either as an X-ray photon or transferred to another electron, which is ejected, from the atom with energy.

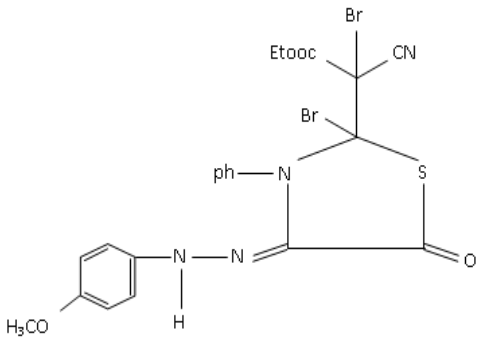
2.4. Inhibitors.

The organic inhibitors used in this study were selected from 1,3-thiazolidin-5-one derivatives and were prepared as before [23,24] and are listed as the following:

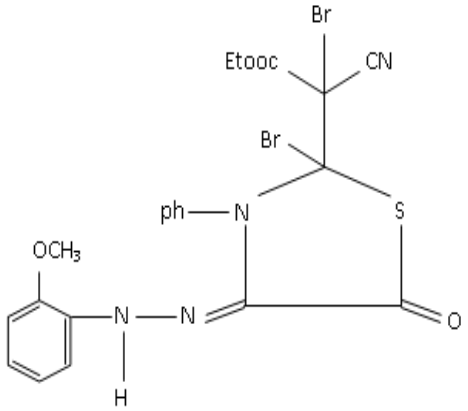
Series (A): compounds 1,2,3

Series (B): compounds 4,5,6

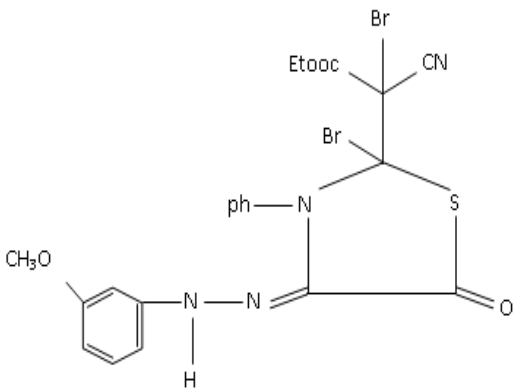
Series (C): compounds 7,8,9,10



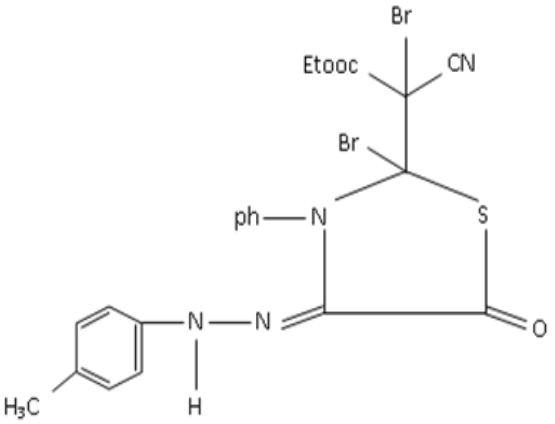
Compound 1
4-(p-methoxyphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one



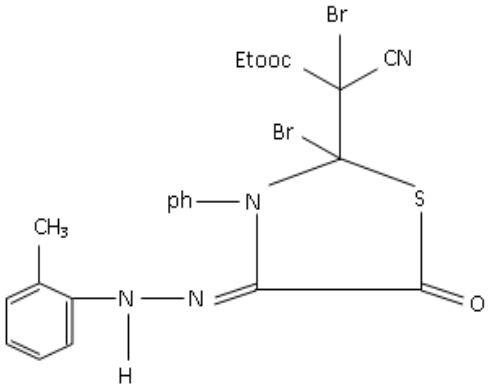
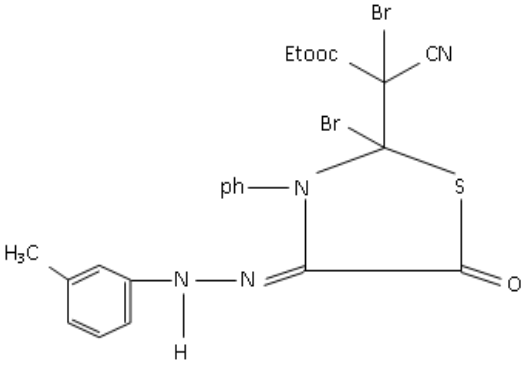
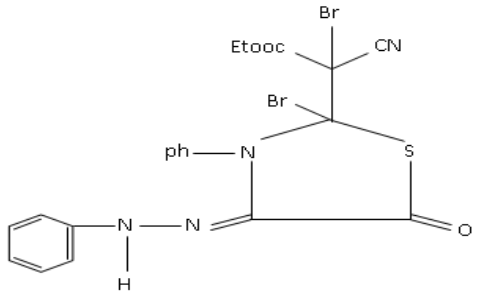
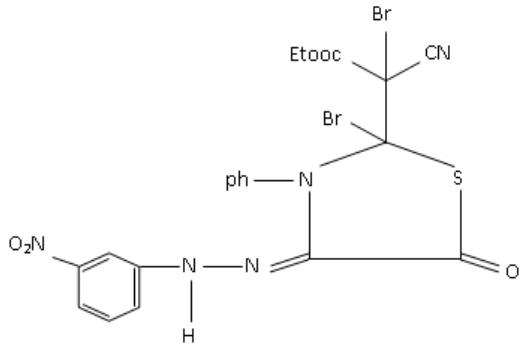
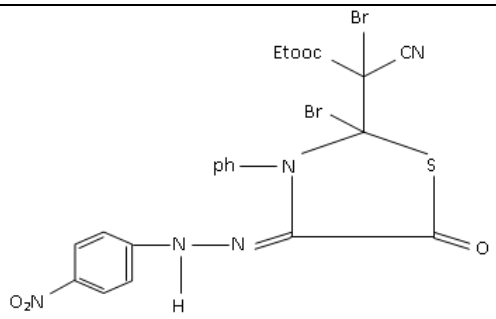
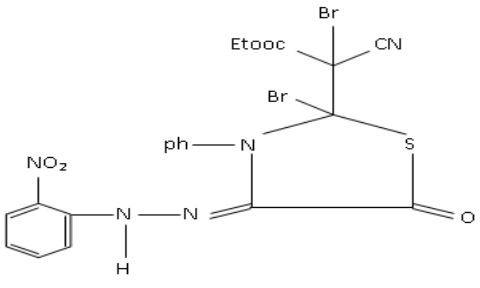
Compound 2
4-(o-methoxyphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one



Compound 3



Compound 4

4-(m-methoxyphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one	4-(p-methylphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one
 **Compound 5** 4-(o-methylphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one	 **Compound 6** 4-(m-methylphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one
 **Compound 7** 4-phenylazo-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one	 **Compound 8** 4-(m-nitrophenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one
 **Compound 9** 4-(p-nitrophenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one	 **Compound 10** 4-(o-nitrophenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one

3. RESULTS AND DISCUSSION

3.1 Weight-loss technique.

3.1.1 Effect of inhibitor concentration

Fig.1 represents the weight loss-time curves of 316 SS in 1M HCl devoid of and containing various concentrations of compound 1 at 303K as an example the 1,3-thiazolidin-5-one compounds. Similar curves were obtained for the other compounds not shown. Similar curves were obtained for the other studied compounds not shown. It is seen from this figure that, by increasing the concentration of these compounds, the weight loss values of 316 SS were decreased. This means that the presence of these compounds retards the corrosion of 316 SS in 1M HCl or in other words, these compounds act as corrosion inhibitors.

The linear relationship between the weight loss and time was obtained. This indicates that the absence of insoluble surface films during corrosion [25]. Hence the studied 1,3-thiazolidin-5-one derivatives are first adsorbed on the 316SS 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.

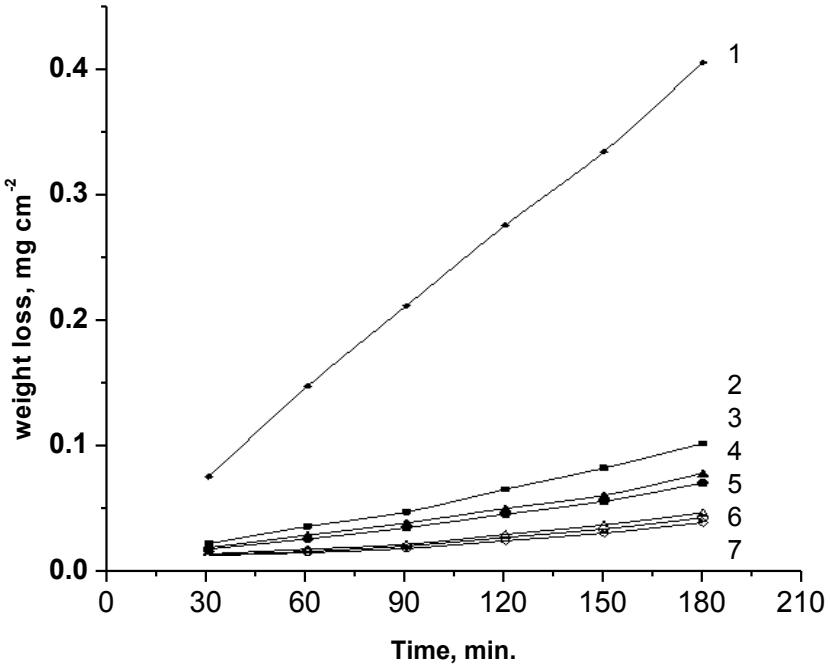


Figure 1. Weight loss-time curves for 316 SS in 1.0 M HCl solution devoid of and containing compound 1 1)0.0M compound 1 2) 3 x 10^{-5} M 3) 7 x 10^{-5} M 4) 3 x 10^{-4} M 5) 7 x 10^{-4} M 6) 3 x 10^{-3} M 7) 7 x 10^{-3}M

The percentage inhibition efficiency (IE%) and the surface coverage (Θ) was computed using the following equations

$$IE\% = [1 - (\Delta W_{add} / \Delta W_{free})] \times 100 \quad (1)$$

$$\Theta = 1 - (\Delta W_{add} / \Delta W_{free}) \quad (2)$$

where, ΔW_{free} and ΔW_{add} are weight losses values in the corrosive medium, and in the inhibited medium at given time values and temperature.

The values of the percentage inhibition efficiency (%IE) of 316 SS in the presence of different concentrations of 1,3-thiazolidin-5-one derivatives at 303K was inserted in Table1 (A&B). It is clearly that all the values of the percentage inhibition efficiency (%IE) increase by increasing the concentration of the studied 1,3-thiazolidin-5-one derivatives. The order of the inhibition efficiencies of 1,3-thiazolidin-5-one derivatives are:

Series (A) > Series **(B)** > **Series (C)**

Series (A) : (1) > (2) > (3) Series (B) : (4) > (5) > (6) Series (C): (7) > (8) > (9) > (10)

This sequence will be explained later

Table (1.A). Percentage inhibition efficiency at different concentrations of inhibitors(1-5) as determined from weight loss method in 1M HCl at 30 ^{o}C.

Conc., M	1	2	3	4	5
3 x 10^{-5}	82.0	77.4	75.2	58.7	60.3
7 x 10^{-5}	86.3	79.1	78.7	61.0	60.2
3 x 10^{-4}	88.3	81.5	82.6	71.3	70.5
7 x 10^{-4}	94.9	85.1	83.3	75.3	74.9
3 x 10^{-3}	94.9	86.3	87.9	82.8	81.5
7 x 10^{-3}	95.5	90.2	88.6	87.2	86.0

Table (1.B). Percentage inhibition efficiency at different concentrations of inhibitors(6-10) as determined from weight loss method in 1M HCl at 30 ^{o}C.

Conc., M	6	7	8	9	10
3 x 10^{-5}	60.9	58.3	56.3	55.1	54.3
7 x 10^{-5}	63.7	62.4	58.9	58.3	57.9
3 x 10^{-4}	72.0	65.7	64.3	62.6	58.5
7 x 10^{-4}	73.5	68.9	69.2	64.8	60.7
3 x 10^{-3}	79.7	77.2	71.4	68.5	65.3
7 x 10^{-3}	82.0	81.0	77.0	75.0	71.3

3.1.2 Adsorption isotherms.

The adsorption of 1,3-thiazolidin-5-one derivatives at the 316SS surface is regarded as a substitute adsorption process between the thiazolidin compounds in the aqueous phase (Th_{aq}) and the water molecules adsorbed on the electrode surface (H_2O_{aq}),

$$Th_{aq} + XH_2O_{aq} = Th_{aq} + H_2O_{aq} \quad (3)$$

where, X is the ratio of the number of water molecules replaced by one molecule of thiazolidin derivatives adsorbate. The adsorption process depends on the chemical structure of the thiazolidin compounds, the type of the stainless steel used, the nature of its surface, the nature of the corrosion electrolyte, the pH value, the temperature and the electrochemical potential of the metal-solution interface [26]. To choose the suitable isotherm, the values of surface coverage, θ, for different concentration of the studied compounds are applied to several adsorption isotherms such as Temkin, Frumkin, Frundlich and Langumir. The best results were obtained obeys the Temkin's adsorption isotherm [27], according to the following equation:

$$\ln K C = a \theta \quad (4)$$

where, θ: is the degree of surface coverage,

a: is the molecule interaction parameter depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the metal surface, C: is the inhibitor concentration in the bulk solution, K: is the equilibrium constant of the adsorption reaction and it is related to the standard free energy of adsorption ($\Delta G°_{ads.}$) by:

$$K = \frac{1}{55.5} \exp\left[\frac{-\Delta G^{o}_{ads}}{RT} \right] \quad (5)$$

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

Fig .2 shows the variation of the degree of surface coverage (θ with log C) for the 316 SS in the presence of series A as an example of thiazolidin derivatives. Similar figures were obtained from series B and C not shown. Straight lines were obtained. This means that the adsorption of 1,3-thiazolidin-5-one derivatives obeys the Temkin's adsorption isotherm. This is suggested that the thiazolidin derivatives block the reaction sites on the surface of 316SS samples by adsorption [28] and reduces the available area for further corrosion reaction.

On the other hand, it is found that the kinetic-thermodynamic model of El-Awady et. al. [29]:

$$\log \theta / (1-\theta) = \log K' + y \log C \quad (6)$$

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 only one 1,3-thiazolidin-5-one derivatives molecule and (C) is the bulk concentration of the inhibitor. Fig 3 shows the relation between log θ/(1-θ) against logC for series A at 303K as an example of thiazolidin derivatives.Similar figures were obtained from series B and C not shown. Straight line relationships were obtained suggesting the validity of this model for all cases studied. The calculated values of 1/y, K and $\Delta G°_{ads.}$ are given in Table 2. Inspection of the data of this Table shows that the values of ($\Delta G°_{ads.}$) are negative sign. This indicate that the adsorption of 1,3-thiazolidin-5-one derivatives on the surface of 316SS is proceeding spontaneously and is accompanied by a highly efficient adsorption. It is worth noting that the value of

1/y is less than unity. This means that the given inhibitor molecules will not occupy more than one active site. In general, the values of $\Delta G°_{ads.}$) obtained from El-Awady model is very close to the values obtained from Temkin's adsorption isotherms.

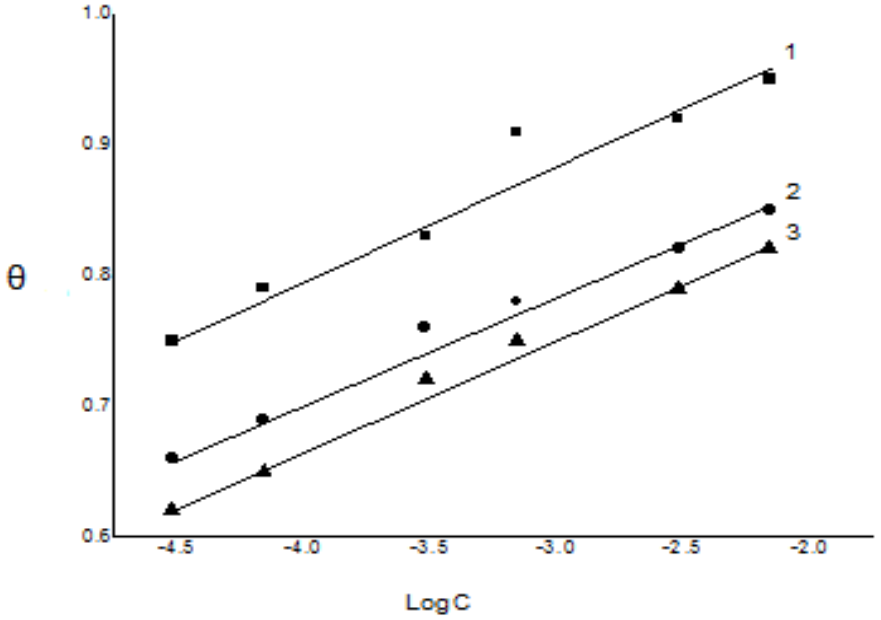


Figure 2. The relation between the degree of surface coverage (θ) and (log C) in the presence of compounds 1-3.(Temkin adsorption isotherm)

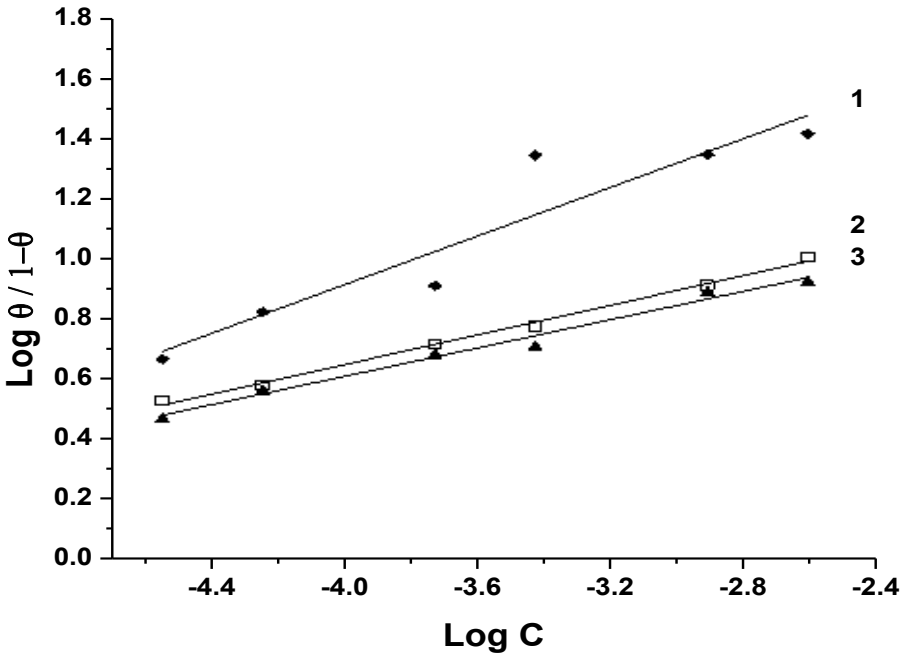


Figure 3. The relation between log θ/(1-θ) against logC in the presence of various concentrations of compounds 1-3.

Table 2. The equilibrium constant of adsorption (K), Free energy of adsorption ($\Delta G^{o}_{ads.}$),and number of surface active sites(1/y) for all 1,3-thiazolidin-5-one derivatives From weight loss method at 30°C.

Inhibitors	Kinetic model			Temkin isotherm	
	1/y	K X10^{-2}	$-\Delta G^{o}_{ads.}$, kJ mol^{-1}	KX10^{-2}	$-\Delta G^{o}_{ads.}$, kJ mol^{-1}
Inhibitor (1)	3.5	105.2	58.1	95.0	57.3
Inhibitor (2)	5.3	96.1	55.3	88.4	56.8
Inhibitor (3)	4.4	94.4	50.2	77.0	51.8
Inhibitor (4)	3.2	77.6	42.8	71.0	45.0
Inhibitor (5)	4.6	68.1	41.4	69.0	42.3
Inhibitor (6)	4.0	63.3	36.4	53.7	39.7
Inhibitor (7)	5.1	52.6	33.2	49.0	35.4
Inhibitor (8)	7.3	44.4	28.8	43.2	31.5
Inhibitor (9)	7.8	41.5	22.5	36.5	28.4
Inhibitor (10)	6.9	31.8	19.9	29.9	25.2

3.2- Electrochemical Impedance Spectroscopy (EIS)

Fig.4 shows the Nyquist plots of 316SS in 1M HCl solution devoid of and containing various concentrations of compound 1 as an example the 1,3-thiazolidin-5-one compounds. Similar curves were obtained for the other compounds not shown. An EIS was conducted at OCP after 15 minutes' immersion in the test solution and at frequency range from 10kHz to 100MHz. The equivalent circuit proposed by Randles as shown in Fig. 5, used in this study. This model consists of the solution resistance (R_s), the charge-transfer resistance of the interface corrosion reaction (R_t) and the double layer capacitance (C_{dl}). It obvious from Fig.4, that the impedance diagram in most cases does not show perfect semicircles. This behavior can be attributed to the frequency dispersions as a result of roughness and inhomogeneity of the 316SS surface [30-32]. As the concentration of the additive increases, the diameters of the semicircles increase. This indicates that, the increase in the protective properties of the 316 SS surface and the corrosion of it is mainly controlled by a charge transfer process. Thus, the capacitive semicircle is correlated with the dielectric properties and the thickness of barrier adsorbed film.

The values of R_s and R_t, can be obtained from the intercepts of the semicircle with the axis of the real component. C_{dl} can be calculated from the angular frequency ($\omega = 2\pi f$) at the maximum imaginary component and the charge transfer resistance according to the following equation:

$$C_{dl} = [1/\omega_{max} . R_p] = [1/2\pi . f_{max} . R_p] \quad (8)$$

where, f is frequency, ω is the angular velocity

The percentage inhibition (%IE) was calculated in the presence of the 1,3-thiazolidin-5-one compounds from the following equations:

$$\%IE = \left(1 - \frac{(R_t)_{free}}{(R_t)_{add.}}\right) x100 \quad (9)$$

where, $(R_t)_{free}$ = charge transfer resistance in the blank solution.

$(R_t)_{add.}$ = charge transfer resistance in the presence of additive.

The impedance parameters such as, R_t, which is equivalent to R_p, C_{dl}. and %IE are derived from the Nyquist plots and given in Table 3. It is observed that the values of R_t increase with increasing the concentration of the inhibitors and this in turn leads to a decrease in corrosion rate of 316SS in 1M HCl acid solution. The values of double layer capacitance, C_{dl}, decrease with increasing the concentration of the additives. A low capacitance may result if organic inhibitor molecules of lower dielectric constant through adsorption replace water molecules at the electrode interface. When such low capacitance values in connection with high R_t values, it is apparent that a relationship exists between adsorption and inhibition.

From the data given in Table 3, the order of decreasing inhibition efficiency for the used thiazolidin derivatives is: -

Series (A) > Series (B) > Series (C)

Where, Series (A):1 > 2 > 3 Series (B): 4 >5 > 6 Series (C): 7 > 8 > 9 >10

Apparently, the results obtained from EIS technique give further support to the results predicted from weight loss technique. These results confirm the previous suggestion that these compounds are adsorbed on the metal surface.

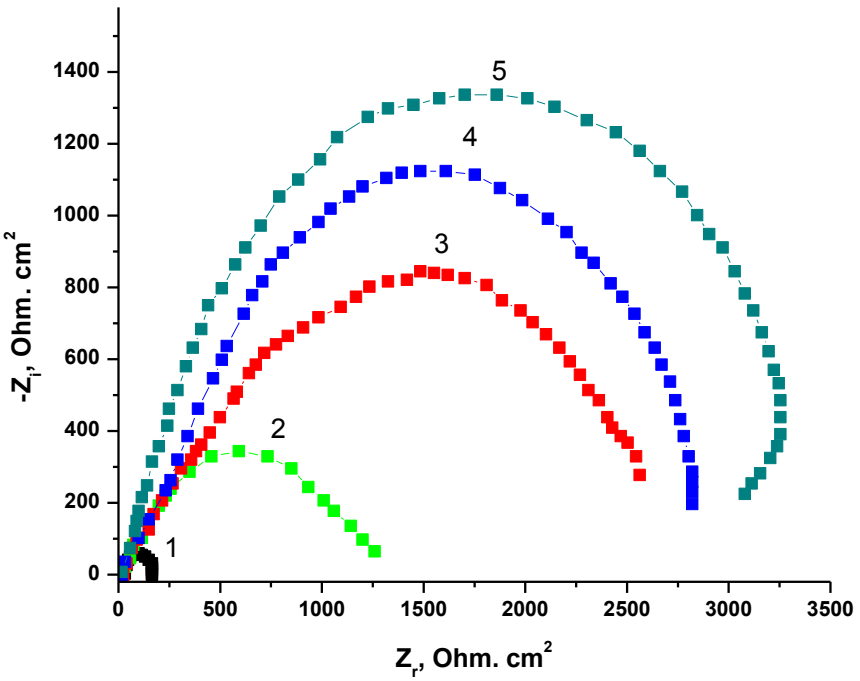


Figure 4. The Nyquist plots of 316SS in 1M HCl solution devoid of and containing various concentrations of compound 1 1)0.0M compound 1 2) 3 x 10^{-4} M 3) 7 x 10^{-4} M 4) 3 x 10^{-3} M 5) 7 x 10^{-3} M

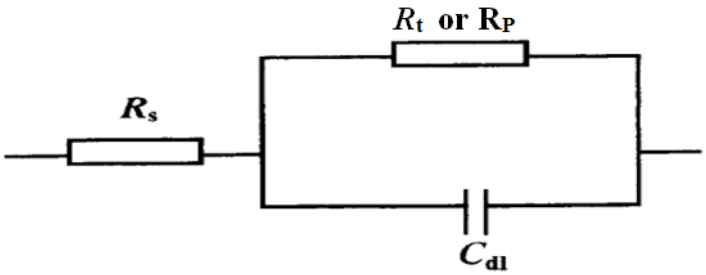


Figure 5. Equivalent electronic circuit for a simple electrochemical cell.

Table 3. Data obtained from EIS measurements of 316L SS in 1 M HCl in the presence and absence of different concentrations concentrations of 1,3-thiazolidin-5-one derivatives

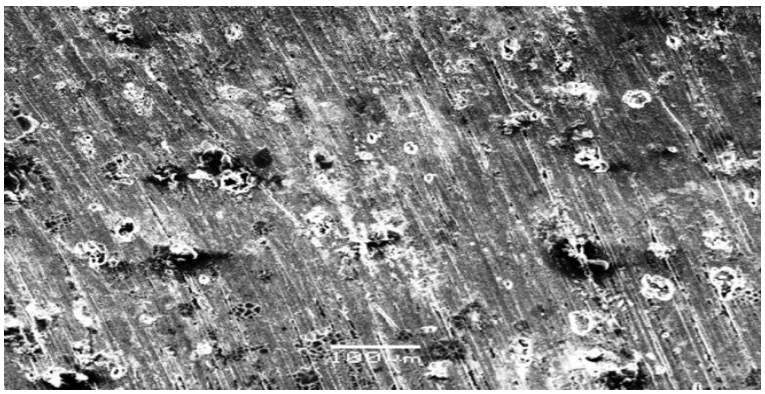
Inhibitors	R_t, ohm. cm^2	$C_{dl.}$ µF. cm^2	% IE
Blank (1MHCl)	143.2	129.7	
3×10^{-4}compound1	1173.9	6.4	87.8
7×10^{-4} compound1	2604.0	0.8	94.5
3×10^{-3} compound1	2754.2	0.5	94.8
7×10^{-3} compound1	3182.7	0.4	95.5
3×10^{-4}compound2	873.3	10.9	83.6
7×10^{-4} compound2	1136.7	6.2	87.4
3×10^{-3} compound2	1093.3	5.5	86.9
7×10^{-3} compound2	1790.3	2.8	92.0
3×10^{-4}compound3	906.5	11.6	84.2
7×10^{-4} compound3	1008.6	8.1	85.8
3×10^{-3} compound3	1110.2	5.8	87.1
7×10^{-3} compound3	1193.5	4.4	88.0
3×10^{-4}compound4	502.5	26.4	71.5
7×10^{-4} compound4	577.5	15.1	75.2
3×10^{-3} compound4	791.3	2.4	81.9
7×10^{-3} compound4	981.0	1.4	85.4
3×10^{-4}compound5	540.5	17.1	73.5
7×10^{-4} compound5	591.8	16.7	75.8
3×10^{-3} compound5	889.6	4.5	83.9
7×10^{-3} compound1	912.2	5.4	84.3
3×10^{-4}compound6	499.0	25.4	71.3
7×10^{-4} compound6	544.6	20.4	73.7
3×10^{-3} compound6	666.1	14.7	78.5
7×10^{-3} compound6	761.8	6.8	81.2
3×10^{-4}compound7	444.8	28.0	67.8
7×10^{-4} compound7	488.8	22.9	70.7

3 x 10^{-3} compound7	639.4	15.6	77.6
7 x 10^{-3} compound7	723.3	8.9	80.2
3 x 10^{-4}compound8	385.0	40.0	62.8
7 x 10^{-4} compound8	451.8	25.0	68.3
3 x 10^{-3} compound8	479.0	19.7	70.1
7 x 10^{-3} compound8	614.7	10.4	76.7
3 x 10^{-4}compound9	373.0	35.5	61.6
7 x 10^{-4} compound9	423.7	25.1	66.2
3 x 10^{-3} compound9	462.0	22.6	69.0
7 x 10^{-3} compound9	561.7	10.0	74.5
3 x 10^{-4}compound10	359.9	28.3	60.2
7 x 10^{-4} compound10	385.0	35.6	62.8
3 x 10^{-3} compound10	459.0	24.6	68. 8
7 x 10^{-3} compound10	534.4	16.4	73.2

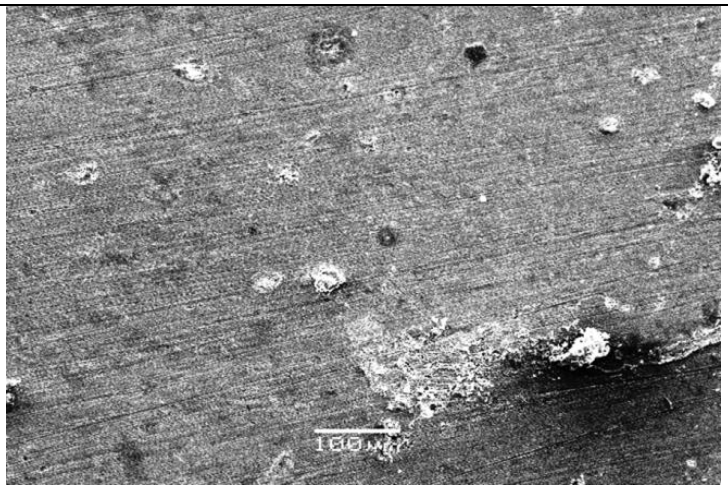
3.3. Scanning electron microscopy (SEM)

The morphology of the corroded 316SS surface of each specimen was studied using scanning electron microscope (SEM). All micrographs of corroded specimens were taken at a magnification of (x500). All the investigated specimens had been naturally immersed for one hour in the test solutions and subjected to electrochemical impedance spectroscopy.

Fig 6[A & B] shows that the SEM of 316SS after immersing for one hour in 1M HCl solution in the absence and presence of 7x10^{-3}M of compound 1 as an example the 1,3-thiazolidin-5-one compounds. Similar curves were obtained for the other studied compounds not shown.



A



B

Figure 6. SEM. micrograph (x500) of 316SS after immersed in A) 1M HCl B) 1M HCl + $7x10^{-3}$ M of compound1

From Fig 6A (in absence of inhibitor) the micrographs show an extensive etching composed of greenish and dark areas in the presence of some white areas. According to Rollason[33] the greenish areas reflect the part of protective film which contains mainly chromium and its oxides, where the white areas represent the ferrite phase and the dark areas represent the pearlite, [mixture of ferrite and cementite (Fe_3C)] in a lamellar form. In the presence of $7x10^{-3}$ M of inhibitor 1 (Fig 6 B) there is much less damage to the surface presumably as a result of the formation of the protective film of the inhibitor on the surface of 316SS. The protective film appears to be very smooth and to cover the whole surface without any flaws. This confirms the observed high percentage inhibition efficiency (%IE) of compound 1.

3.4. Energy dispersive X-ray

Fig 7[A & B] shows the surface analysis of 316SS uses energy dispersive X-ray (EDX) after immersed in the absence and presence of $7x10^{-3}$M of compound 1 as an example of the 1,3-thiazolidin-5-one compounds. Similar curves were obtained for the other studied compounds not shown. The results were plotted on a graph of dN/dE *v*s. electron energy. Various peaks owing to different elements were appeared. The results were achieved for 316SS surfaces immersed for one hour in the test solutions and subjected to the electrochemical measurements. From all the obtained analysis charts, it was found that the results of EDX may be explained and discussed depending on the values of weight percentages (wt %) of carbon and chloride atoms on the surface of 316SS as follow:

i. In all the charts of EDX, the carbon atom peak appears around the value of 0.3 KV and the peak of a chloride atom appears at 2.7 KV.

ii- The corrosive medium is 1M HCl solution and the organic additives consist mainly of C, O and/or C, O, N atoms, so the variation of chloride and carbon weight percentages on the surface can be

used quantitively to explain and discuss the adsorption of 1,3-thiazolidin-5-one derivatives of the surface 316 SS.

iii - Fig.7A represents the EDX of 316 SS exposed to 1M HCl at 303K for one hour, where,

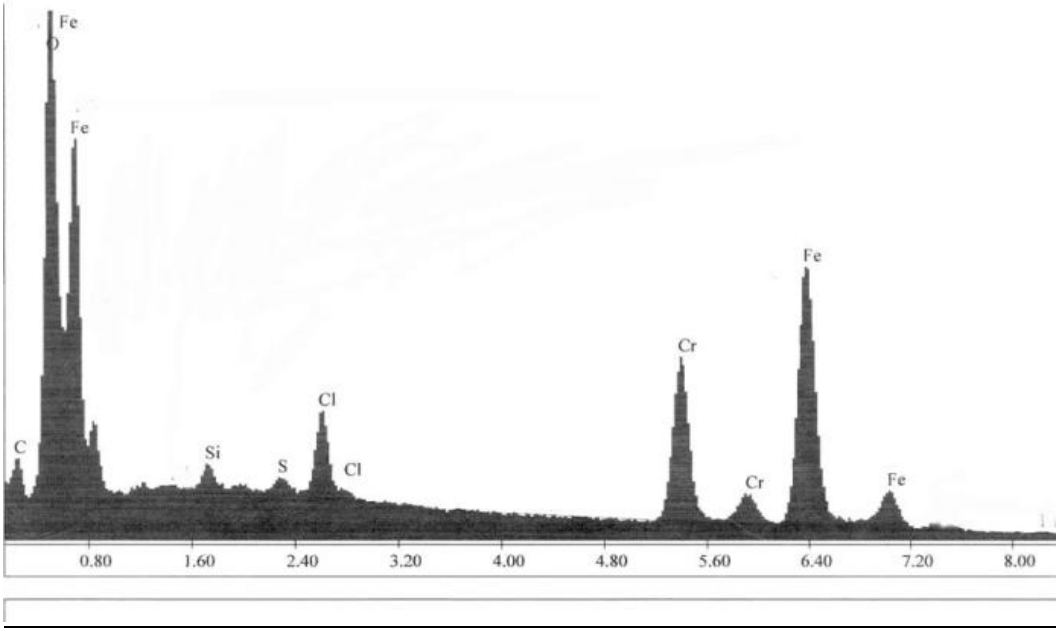
Fig.7 B represents the same sample in the presence of $7x10^{-3}$ M of inhibitor (1). For comparison, it is clearly seen that the weight percentage (wt %) of carbon was increased from (2.2%) to (4.85%), on the other hand the weight percentage (wt %) of chloride was decreased in the presence of inhibitor (1) from (4.5%) to (0.26%) as shown from table 4. By other words, the peak of carbon was increased and the peak of chloride was decreased compared with the corresponding peaks in the absence of inhibitor (1). This is due to the replacement of the firstly adsorbed chloride atoms by C-atoms (inhibitor 1). These results confirm the adsorption of inhibitor (1) on the surface of 316SS

iv. Table 5. summarized the variations of the weight percentages (wt %) of carbon and chloride in the protective films that achieved using EDX for the 316SS in the absence and presence of different types of the investigated 1,3-thiazolidin-5-one derivatives. It is clear that, in all cases the weight percentage values of carbon on the surface were increased by increasing the concentration of the investigated 1,3-thiazolidin-5-one derivatives. On the other hand, the weight percentages (wt %) values of chloride were decreased. This confirms the replacement of the chloride atoms which firstly adsorbed (from 1M HCl) by carbon atoms (from 1,3-thiazolidin-5-one compounds) and hence, the increase in the inhibition efficiency was achieved.

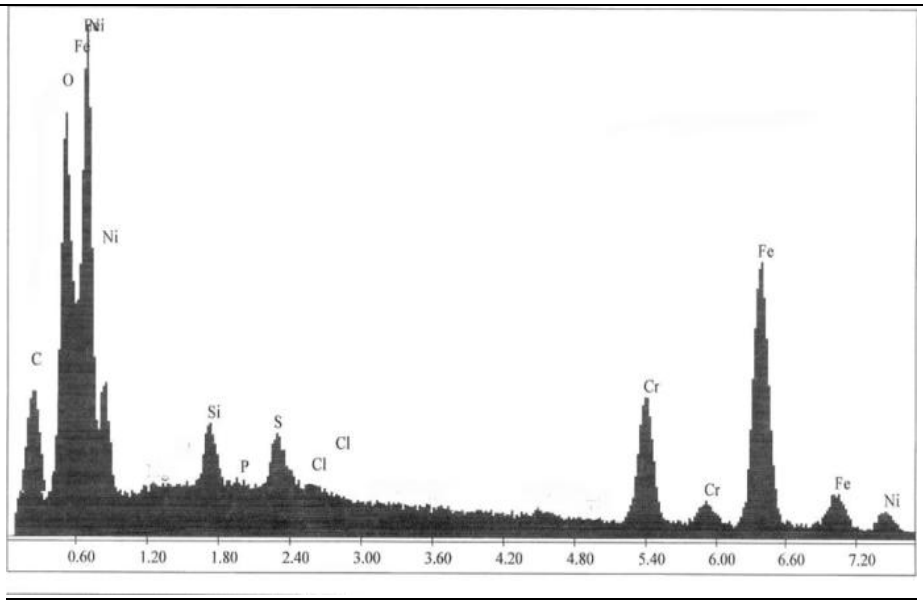
v. The increase in wt % of the carbon atom and decrease wt % of a chloride atom obeys the following sequence:

Series (A) > Series (B) > Series (C)

where Series (A): 1 > 2 > 3 Series (B): 4 >5 > 6 Series (C): 7 > 8 > 9 >10



A



B

Figure 7. EDX analysis of 316SS surface after immersed in A) 1M HCl B) M 1M HCl + $7x10^{-3}$M of compound1

This is also in a good similarity with the observed order of percentage inhibition efficiency, which achieved by weight loss and electrochemical impedance spectroscopy techniques. It is found that the inhibition efficiency of the 1,3-thiazolidin-5-one compounds toward the corrosion of 316L SS in 1 M HCl are more efficient than that obtained by other some inhibitors such as, antibacterial drugs [14],p-aminoazobenzene derivatives [2],heptamolybdate ions[34]and some bis-N,S-bidentate Schiff bases [35].

Table 4. Variation of the weight percentage (wt. %) of carbon and chloride obtained from EDX for 316SS in the absence and presence of 1,3-thiazolidin-5-one derivatives.

Inhibitor 7x10-3	(wt. %) of carbon	(wt. %) of chloride
1M HCl	2.2	4.5
Inhibitor (1)	4.85	0.26
Inhibitor (2)	4.21	0.48
Inhibitor (3)	4.00	0.83
Inhibitor (4)	3.81	0.92
Inhibitor (5)	3.45	1.04
Inhibitor (6)	3.09	1.25

Inhibitor (7)	2.67	1.42
Inhibitor (8)	2.12	1.57
Inhibitor (9)	1.80	1.85
Inhibitor (10)	1.53	1.97

3.5. Chemical structure and corrosion inhibition of stainless steel type 316L.

The inhibition of corrosion of 316SS in 1.0M HCl solution by the investigated **1,3-**thiazolidin-5-one derivatives using weight loss, and AC impedance measurements was found to depend on the concentration, the nature of the inhibitor and the position of the substitutes group in the molecule. Skeletal representation of the proposed mode of adsorption of the investigated 1,3-thiazolidin-5-one compounds as shown in Fig.8 and clearly indicates the active adsorption centers of these compounds on the metal surface. These compounds can be adsorbed in a flat orientation through a tridentate form.

The observations indicate that the corrosion inhibition is due to the adsorption of the inhibitors at the solution interface [36], the nature of the inhibitor interaction on the metal surface during corrosion inhibition can be explained in terms of its adsorption characteristics [37]. However, the inhibition efficiency of additive compounds depends on many factors, which include the number of adsorption active centers in the molecule and their charge density, the molecular size, the mode of adsorption, heat of hydrogenation and the formation of metallic complexes. Variation in the structure of the inhibitor molecules takes place through the position of the phenylhazo group. Therefore, the inhibition efficiency depends on this part of the molecule. Adsorbed molecules on the surface of 316SS interface with cathodic and/or anodic reactions. The inhibition of these reactions would obviously depend on the degree of the surface coverage of the metal with the adsorbate. Competitive adsorption is assumed to occur on the surface of the 316SS between the aggressive Cl^- ions, on one hand, and the inhibitor molecules, on the other. The order of the increasing inhibition efficiency of the tested compounds in 1.0 M HCl for 316SS is:

Series (A) > Series (B) > Series (C).

3.5.1. Effect of substituted group

Known as the inhibition efficiency process depends essentially on the electron density of the active centers. The subsequent step is to follow the effect of substituted group, whether increase and decrease the inhibition efficiency through its effect on the active centers, i.e. electron donating or withdrawing groups e.g. OCH_3, CH_3, NO_2. The three substituted groups investigated are located in para -, meta - and ortho - positions of phenyl ring with respect to the phenylazo molecule derivatives. The inhibition of such derivatives was compared with that of unsubstituted molecule using weight loss and EIS methods, the surface of the 316SS was examined using SEM and EDX. It is obvious that, the percentage inhibition efficiency decreases in the following direction: methoxy- > methyl- > nitro-. Therefore, one can say that the methyl and methoxyl groups increase the electron density of the active centers, consequently, the inhibition efficiency increases. It follows that the methoxyl group is more

efficient than the methyl group. From the structural point of view, both methyl and methoxyl groups have +R effect but the inductive effect is +I and –I, respectively. Although the methyl group has +R, but its effect is very slight as a result of hyperconjugation. In case of methoxyl group, the effect of +R is large and the inductive effect, -I. The inhibition efficiency of the nitro group is the least one, due to its highest electrophilic character, so it comes at the last among the additives used. Because of co-planarity with the aryl ring, maximum electron withdrawal is expected to occur. Possible hydrogenation of the NO_2 group in acid medium on the 316SS surface would also enhance decreased efficiency of the inhibitor, as the released heat of hydrogenation would aid the adsorption of the molecule. Evidence for the validity of the above explanation is gathered from the application of Hammett constant, σ ($\sigma p\text{-}OCH_3$ = -0.27, $\sigma p\text{-}CH_3$ = - 0.17, $\sigma p\text{-}NO_2$ =+0.78)

From the above, the inhibition efficiency of these inhibitors as follows:

Series (A) > Series (B) > Series (C).

3.5.2- Effect of substituted position

It is obvious that from the previous discussions that the corrosion inhibition of 316SS in 1M HCl solution was found to depend on the type of substituted group as well as its position in the molecule. This part deals with the effect of substituted position, para-, ortho-, or meta- for each substituted group. Substituted position on increasing the inhibition efficiency follows the following order:

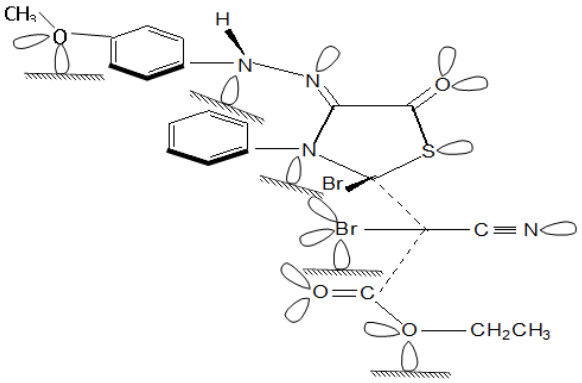
meta- > ortho- > para-

In the light of the above results of inhibition efficiency deduced by the different techniques, the p-substituted derivative for all investigated substituted groups,

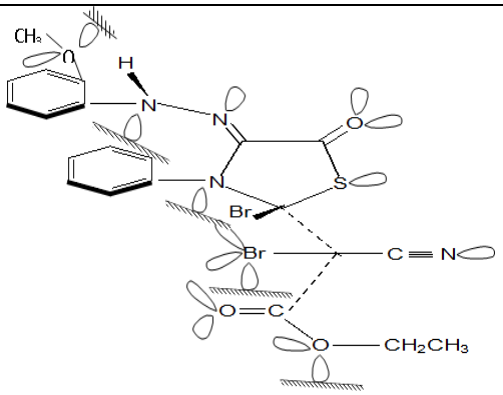
$-OCH_3$, $-CH_3$ or $–NO_2$, occurs a distinct position for inhibition efficiency, owing to the inductive and mesomeric effects which operate together strongly, and this increase the degree of surface coverage and hence the inhibition efficiency.

In case of o-substituted groups the inhibition efficiency decreases owing to the presence of –I (inductive)and +R (resonance) effects but the steric effect complicates the availability of active centers for inhibition reaction, and hence, lower inhibition efficiency than in the case of p-substituted groups.

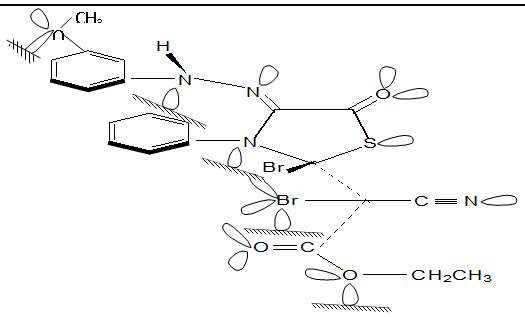
In case of m-substituted groups, the inhibition efficiency depends in the resonance and inductive effects, viz. $–CH_3$ (+R, -I), $-OCH_3$ (+R, -I) and $–NO_2$ (+R, +I) in changing the electron density and the activation of the aromatic ring.



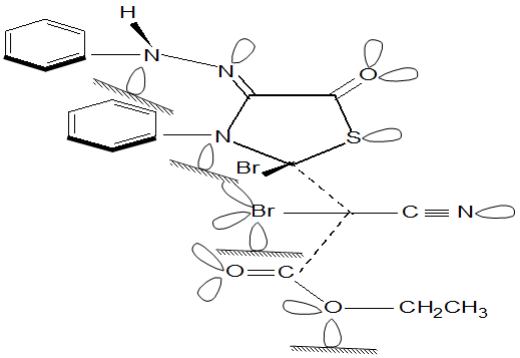
4-(p-methoxyphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one (1)



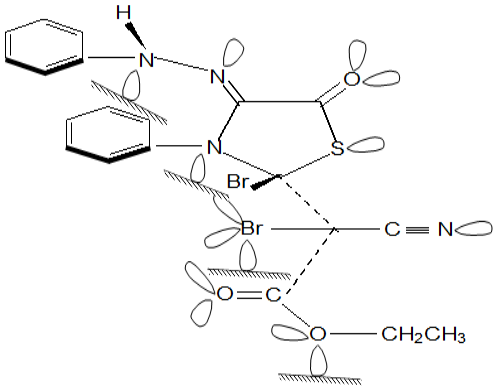
4-(o-methoxyphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one (2)



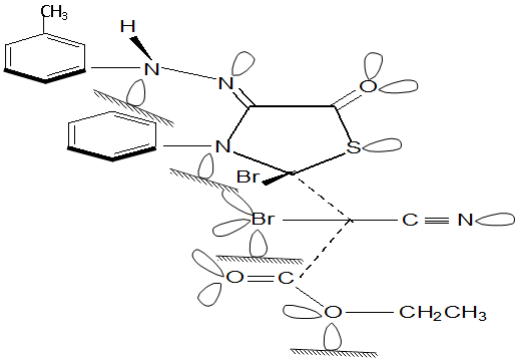
4-(m-methoxyphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one (3)



4-(p-methylphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one (4)



4-(o-methylphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one (5)



4-(m-methylphenylazo)-2-bromo-2-(α-bromoethyl cyanoacetate)-3-phenyl-1,3-thiazolidin-5-one (6)

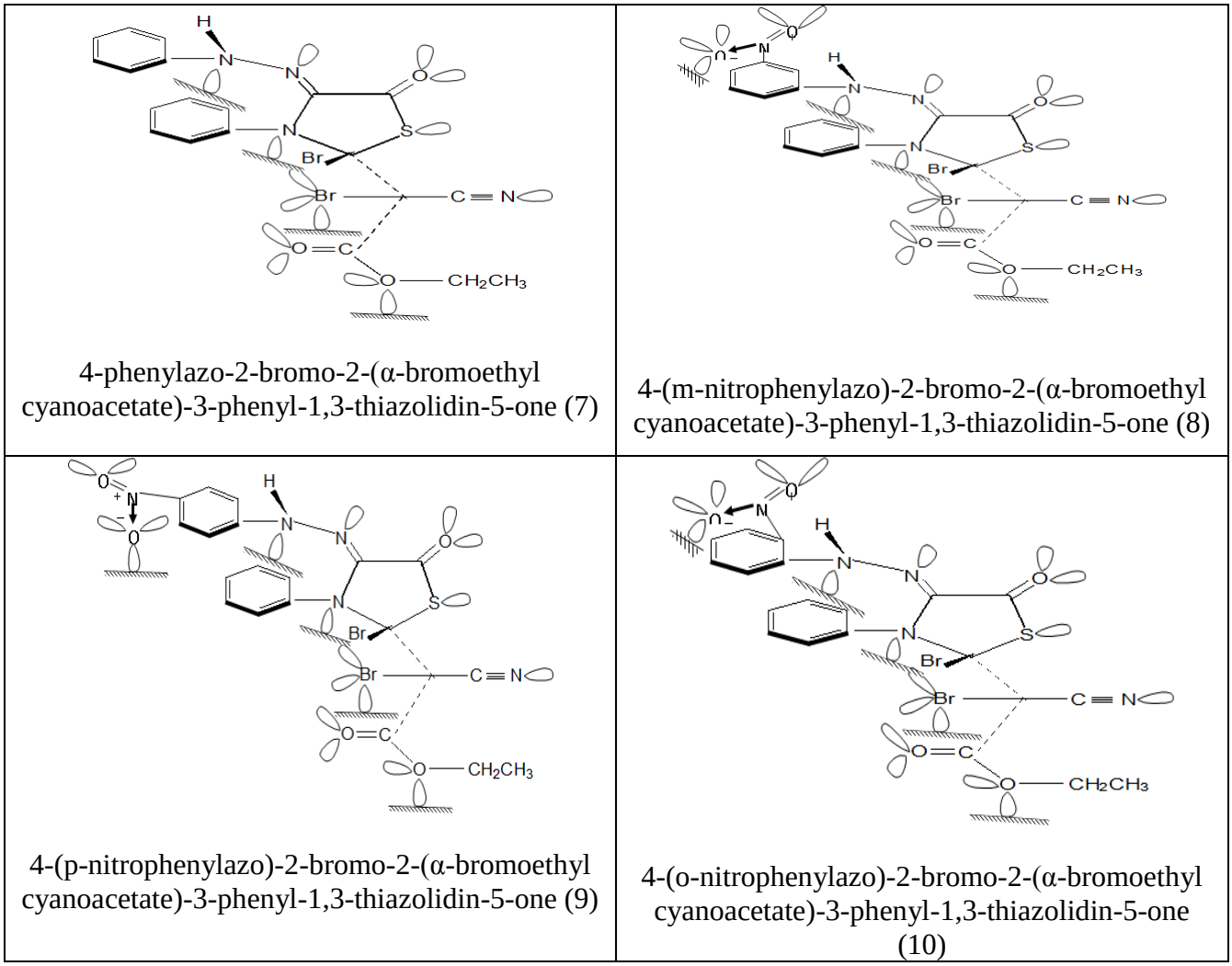


Figure 8. Skeletal representation of the mode of adsorption of 1,3-thiazolidin-5-one derivatives

4. CONCULSIONS

(1) 1,3-thiazolidin-5-one derivatives inhibit the corrosion rate of 316 SS
(2) The adsorption of the studied compounds obeyed Temkin's isotherm.
(3) These compounds are mixed type inhibitors.
(4) SEM indicated that the morphology of 316SS surface in the presence of inhibitors is less damage due to the formation of the smooth protective film
(5) Energy dispersive X-ray revealed quantitively the replacement of the firstly adsorbed chloride atoms by carbon atoms, thereby increasing the inhibition efficiency.
(6) The order of inhibition efficiency depends on the number of active adsorption centers, the type of adsorbed atoms in the molecule and the position of the substitutes group.

References

1. M. Shabani-Nooshabadi, M.S. Ghandchi, *J. Ind. Eng Chem.*, 31 (2015) 231.

2. M. Abdallah, O.A. Hazazi, A.S. Fouda, A.Abdel-Fatah, *Prot. Met. Phys. Chem. Surf*., 51 (2015) 473.
3. M. Mehdipour, B. Ramezanzadeh, S.Y. Arman, *J. Ind. Eng. Chem.*, 21 (2015) 318.
4. M. Abdallah, I. Zaafarany, K.S.Khairou, Y.Emad, *Chem. Tech. Fuels Oils*, 48 (2012) 234.
5. N. Soltani, N. Tavakkoli, M. Khayat Kashani, A. Mosavizadeh,E.E. Oguzie, M.R. Jalali, *J. Ind. Eng Chem*.,20 (2014) 3217.
6. M. Abdallah, A.Y. El-Etre, M. G. Soliman, *Anti Corros. Meth. Mater.*, 53 (2006)118.
7. M. Mehdipour, R. Naderi, B.P. Markhali, *Prog. Org. Coatings*, 77, (2014) 1761.
8. M. Abdallah, A.S. Fouda S.M. Al-Ashry, *Zastita Materijala (Mat.Prot.)* ,49 (2008) 9.
9. A.S. Fouad, M. Abdallah, S.M. Al-Ashry, A.A. Abdel-Fattah, *Desalination*, 250(2010)538.
10. M.Abdallah, *Mater Chem. Phy*., 82 (2003)786.
11. M.Abdallah, S.M. Abd El-Haleem, *Bull Electrochem.* 12 (1996) 449.
12. Ayşegül Öncül, Kerim Çoban, Esma Sezer, Bahire Filiz Şenkal, *Prog. Org. Coatings*, 71 (2011), 167.
13. M. Abdallah, H.M. Al –Tass, B.A.AL Jahdaly, A.S.Fouda, *J Mol. Liq.*, 216 (2016) 590.
14. A. S. Fouda, H. A. Mostafa, H. M. El-Abbasy, *J. Appl .Chem.*, 40 (2010) 1572.
15. M. Abdallah, A.M.El-Dafrawy, M.Sobhi, ,A.H.M. Elwahy, M. R. Shaaban, *Int. J. Electrochem. Sci*.,9 (2014) 2186.
16. M.M. Hamza, S.S. Abd El Rehim, Magdy A.M. Ibrahim, *Arab. J. Chem*., 6 (2013) 413.
17. M. Abdallah, M. E. Moustafa, *Ann. Di Chim. (Italy)* 94 (2004) 601.
18. M. Sobhi, R. El-Sayed, M. Abdallah, *J Surf. Deterg.*, 16 (2013) 937.
19. A. S. Fouda, T. F. Alsawy, E. S. Ahmed, B. S. Abou-elmagd, *Res. Chem. Intermediates* ,39 (2013) 2641.
20. M. Abdallah, H. E Megahed , M.S.Motae , *Monats fur Chemie* 141, (2010)1287.
21. P.B., Mathur, T. Vasudevan, *Corros.* 38 (1982)17.
22. O.A.Hazazi , M. Abdallah, *Int.J.Electrochem Sci*,8(2013)8138.
23. M.A. Metwally, E. Abdel-Latif,F.A. Amer , *J. Text. Assoc*. –Nov. Dec. (2001)155.
24. M.A. Metwally , E. Abdel-Latif ,F.A. Amer , *J. Text. Assoc.* – Nov. Dec., (2002) 149.
25. M. Abdallah, I.A.Zaafarany, B.A.AL Jahdaly , *J. Mater. Env. Sci.*, 7 (2016)1107.
26. M. Abdallah, B. H. Asghar, I. Zaafarany, M. Sobhi, *Prot.Met.Phys Chem .Surf* ,49 (2013) 485.
27. M. Abdallah, H.E.Megahed M.A.Radwan , E.Abdfattah, *J. Amer. Sci* , 8(11) (2012)49.
28. M. Abdallah I.Zaafarany, A.S. Fouda ,D. Abd El-Kader, *J.Mater Eng .Perof.*, 21(2012) 995.
29. Y. A. El-Awady, A. J. Ahmed, *J. Ind. Chem*., 24A (1985)601.
30. M. Sobhi, M. Abdallah, K.S. Khairou, *Monatsh fur Chemie*, 143(2012)1379.
31. E. Bayol, K., Kayakirilmaz, M., Erbil, *Mater.Chem.Phys*., 104 (2007) 74.
32. 3-Jabir H Al-Fahemia, M. Abdallah, Elshafie A. M. Gad, *J Mol. Liquids*,222(2016)1157.
33. B.C. Rollason, *Metallurgy For engineers*, Edward Arnold, London, 3rd ed., (1961).
34. Y.Ait Albrimi, A.Ait Addi, J.Douch,,R.M.Souto, M.Hamdani, *Corros.Sci*.,90 (2015) 522.
35. M.Behapour, S.M.Ghoreishi,, N.Soltani, M.Salavati-Niasari, *Corros.Sci*.,51(2009) 1073.
36. M. Abdallah, Hatem M.Eltass .M.A. Hegazy, H. Ahmed, *Prot. Met. Phys. Chem*. surf.,52 (2016)721.
37. T. Maurakawa, Kato, S.Nagura ,N. Hackerman, *Corros. Sci*., 8 (1968) 483.