

## Inhibitive action of some 3-thiazinonyl-bicyclo[4.2.0] octene-carboxylate derivatives drugs on the corrosion of SS type 304 in 1M HCl solution

*The effect of 3-Thiazinonyl-bicyclo[4.2.0]octene-carboxylate derivatives drugs on the corrosion behavior of 304 stainless steel in 1.0 M hydrochloric acid solution as corrosive medium has been investigated using weight loss and potentiostatic polarization techniques. Some corrosion parameters such as anodic and cathodic Tafel slope, corrosion potential, corrosion current, surface coverage and inhibition efficiency were calculated. The polarization measurements indicated that the inhibitors are of anodic type and inhibit corrosion by adsorption on the surface of steel due to the presence of more than one active centre in the inhibitor molecule. The adsorption is obeyed Langmuir adsorption isotherm. The activation energy and thermodynamic parameters were calculated in the temperature range 25–55°C. It was found that the corrosion rate increases with temperature and the inhibition efficiency decreases with increasing temperature.*

**Key words:** 304 stainless steel, corrosion, chloride solution, 3-Thiazinonyl-bicyclo[4.2.0] octene-carboxylate

### 1. INTRODUCTION

Stainless steel type 304 has found wide applications in variety of industries. It is covered with a highly protective film of chromium ox hydroxide and is resistant to corrosion in many aggressive environments. Hydrochloric acid solution, however, readily attack SS. It is possible to reduce the corrosion rate to safe level by adding inhibitors. Organic compounds and their derivatives were used successfully as inhibitors for different types of steels and were studied extensively through the last century. Recently, interest is still growing for exploiting other inhibitors for the corrosion of stainless steels [1]. Several organic molecules containing sulfur and nitrogen heteroatoms were suggested as inhibitors for steel in acidic medium [2]. The inhibition mechanism for this class of inhibitors is mainly based on adsorption [3]. Generally a stronger co-ordination bond cause higher inhibition efficiency.

The present investigation aimed to study the effect of three 3-thiazinonyl-bicyclo[4.2.0]octene-carboxylate derivatives as corrosion inhibitors for SS type 304 dissolution in 1 M HCl using two methods. The effect of temperature on the dissolution of SS type in 1 M HCl containing  $5 \times 10^{-4}$  M of the investigated inhibitors was also studied.

### 2. EXPERIMENTAL TECHNIQUES

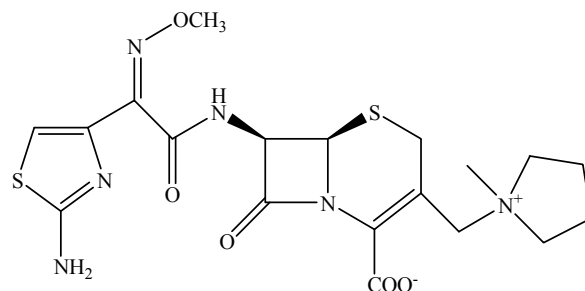
Stainless steel type 304 specimens were in the form of rods and sheets. The sheets of 2 x 2 x 2 cm

size were used for weight loss measurements. For potentiodynamic studies, working electrodes with surface area of  $1 \text{ cm}^2$  were mounted to a glass cell in the form of a cylinder. The electrode was polished with different grades of emery paper, degreased with acetone and rinsed by distilled water. Weight loss measurements were carried out as described elsewhere [4]. The specimens are immersed in 100 ml of test solution for period of 6 h. In potentiodynamic polarization measurements, the electrode potential was measured against a saturated calomel electrode (SCE). A platinum electrode was used as an auxiliary electrode.  $10^{-3}$  M stock solutions were used from these compounds.

The following three 3-thiazinonyl-bicyclo[4.2.0] octene-carboxylate derivatives drugs were used as inhibitors for the corrosion of SS type 304 in 1M HCl:

(6R,7R,Z)-7-(2-(2-aminothiazol-4-yl)-2-(methoxyimino)acetamido)-3-((1-methyl pyrrolidinium-1-yl)methyl)-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylate

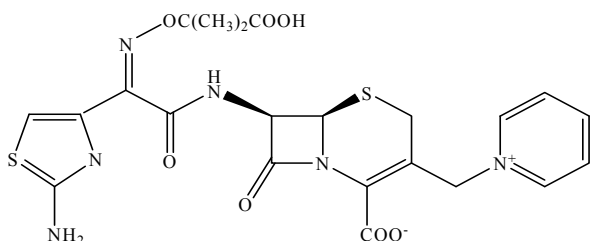
(Produced by Bristol-Myers Squibb Egypt Company)



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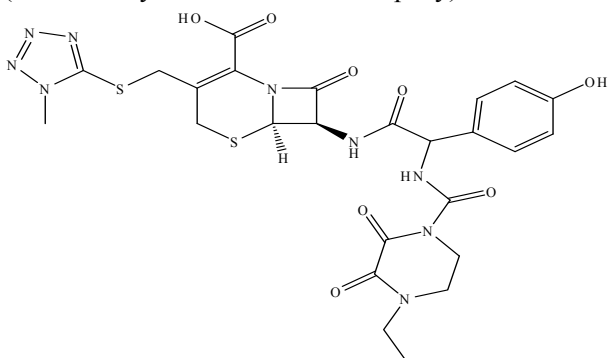
B-(6R,7R,Z)-7-(2-(2-aminothiazol-4-yl)-2-(2-carboxypropan-2-yloxyimino)acetamido)-8-oxo-3-(pyridinium-1-ylmethyl)-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylate

(Produced by Glaxo Smithkline Company)



C-(6R,7R,Z)-7-([2-[(4-ethyl-2,3-dioxo-piperazine-1-carbonyl)amino]-2-(4-hydroxyphenyl) acetyl];amino]-3-[(1-methyltetrazol-5-yl)sulfanylmethyl]-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylic acid

(Produced by Pharmaceutical Company)



### 3. RESULTS AND DISCUSSION

#### 3.1. Weight loss measurements

Stainless steel type 304 species were exposed for 6 h in 1M HCl with and without addition of the inhibitors. From the value of weight loss the percent of inhibition efficiency (%IE) at each inhibitor concentration was calculated using the equation:

$$\%IE = [1 - (w_{dd} / w_{free})] \times 100 \quad (1)$$

where  $w_{add}$  and  $w_{free}$  are the weight losses of the metal in presence and absence of the inhibitors, respectively. The results are collected in Table 1. It is obvious that, the %IE increases with increasing the inhibitor concentration, whereas decreases in the following order: compound C > compound B > compound A. Weight loss-time curves for the corrosion of SS type 304 in 1M HCl in absence and presence of different concentrations of compound (C) at 25°C are shown in Fig. 1.

#### 3.1.1- adsorption isotherm

The plot of  $(C/\theta)$  against C was made to confirm the Langmuir isotherm and its given in Fig. 2. The

Langmuir adsorption isotherm [5] may express by:

$$\theta / 1 - \theta = AC \exp (-Q / RT) \quad (2)$$

where T is temperature, A is independent constant, C is inhibitor concentration, R is gas constant, Q is heat of adsorption and  $\theta$  is surface covered by the inhibitor molecule. On the other hand, it is found that the kinetic-thermodynamic model of El-Awady et al [6].

$$\log (\theta / 1 - \theta) = \log k' + y \log C \quad (3)$$

is valid to operate the present adsorption data. The equilibrium constant of adsorption  $K = K'^{(1/y)}$ , where  $1/y$  is the number of the surface active sites occupied by one inhibitor molecule and C is the bulk concentration of the inhibitor. Plotting  $\log (\theta / 1 - \theta)$  against  $\log C$  for the compounds is given in Fig. 3 where straight-line relationships were obtained suggesting the validity of this model for the studied case. The values of K and  $\Delta G_{ads}^{\circ}$  calculated by Langmuir isotherm and  $1/y$ , K and  $\Delta G_{ads}^{\circ}$  calculated by the kinetic model are given in Table 1. The large values of  $\Delta G_{ads}^{\circ}$  and its negative sign, indicate that the adsorption of these compounds on stainless steel type 304 surface is proceeding spontaneously and is accompanied by a highly efficient adsorption. It is noting that the value of  $1/y$  is more than unity. This means that the given inhibitor molecules will form monolayer on the steel surface. In general the values of  $\Delta G_{ads}^{\circ}$  obtained from El Awady [7] et al model are comparable with those obtained from Langmuir isotherms. A plot of  $\log (\theta / 1 - \theta)$  vs.  $1/T$  at constant additives concentration ( $5 \times 10^{-5}$  M) is shown in Fig. 4. The Q values were obtained from the slopes of these lines and are given in Table 1. The negative values of Q indicate that the adsorption of the additives on SS type 304 surface in 1 M HCl is exothermic process.

Table 1 - Equilibrium constant (K), free energy of binding ( $\Delta G_{ads}$ ), number of active sites (1/y) for the corrosion of 304 stainless steel in 1 M HCl solution

Inhibitors	Kinetic model			Langmuir isotherm		
	1/y	K	$-\Delta G_{ads}^{\circ}$ (kJ mol <sup>-1</sup> )	K	$-\Delta G_{ads}^{\circ}$ (kJ mol <sup>-1</sup> )	-Q (kJ mol <sup>-1</sup> )
(A)	2.09648	207556	40.291	200023	40.200	15.034
(B)	2.62398	600667	42.925	406461	41.957	16.565
(C)	2.08355	919468	43.979	477998	42.359	23.608

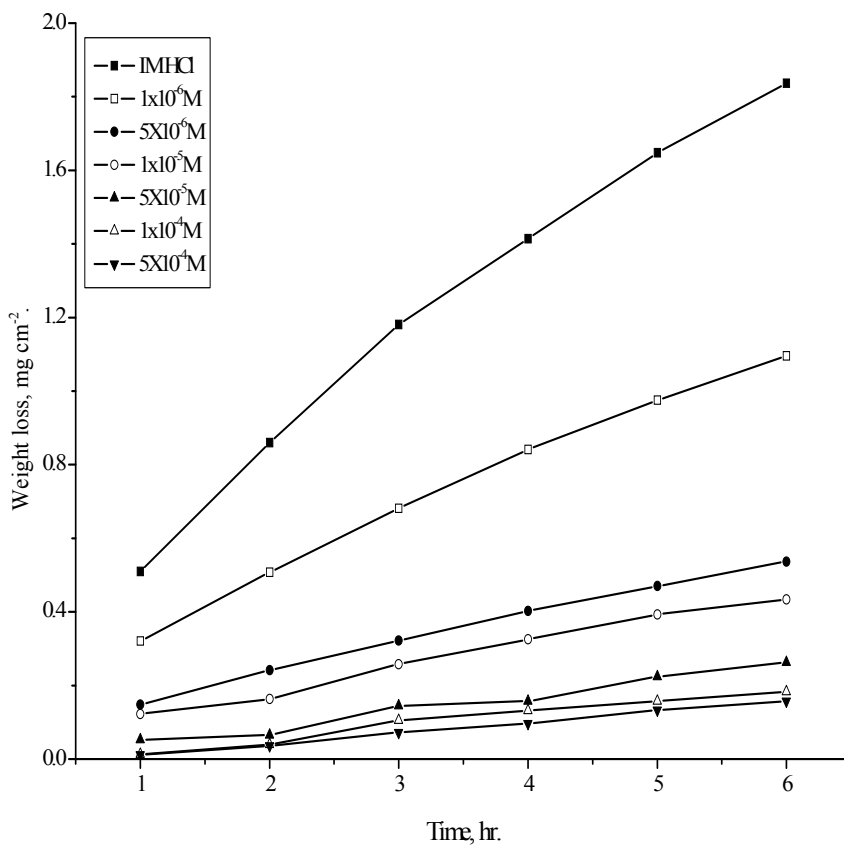


Fig. 1 - Weight loss-time curves for the corrosion of SS type 304 in 1M HCl in absence and presence of different concentrations of inhibitor (C) at 25°C

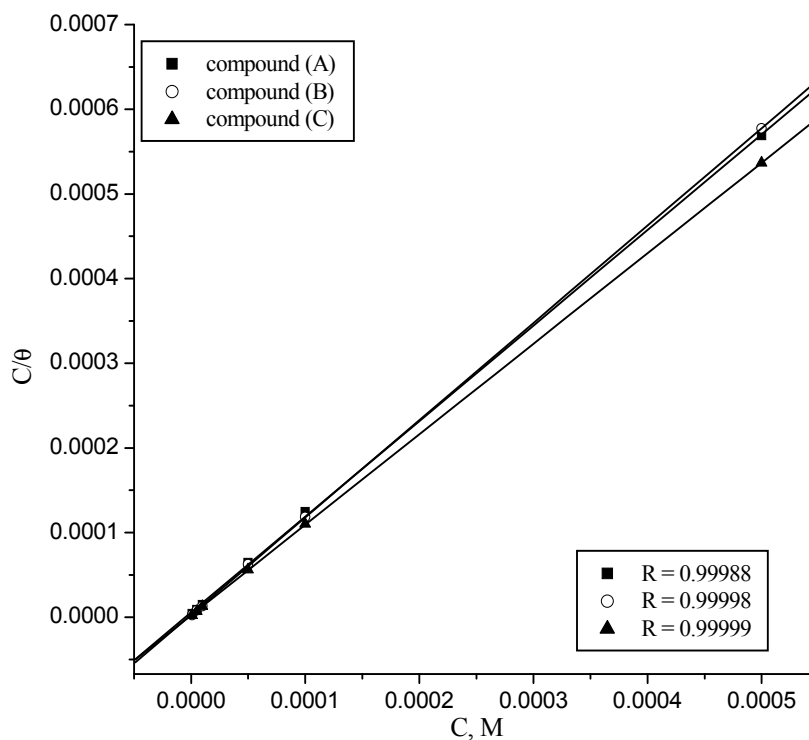


Fig. 2 – Langmuir adsorption isotherm plotted as (C/θ) vs C at 25°C

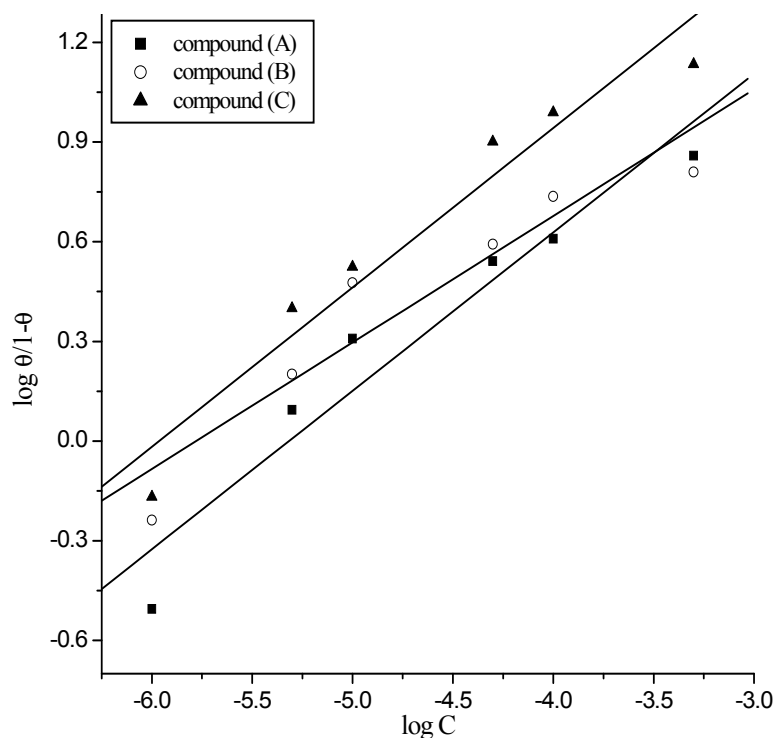


Fig. 3 –  $\log (\theta/1-\theta)$  vs  $C$  for all inhibitors used at  $25^{\circ}\text{C}$

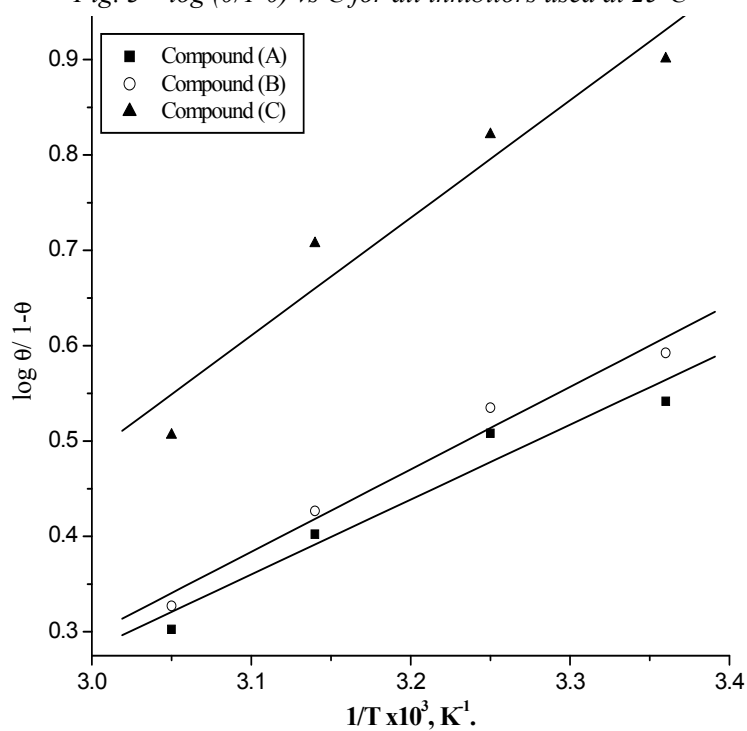


Fig. 4 – plots of  $\log (\theta/1-\theta)$  vs  $1/T$  for  $5 \times 10^{-5} \text{ M}$  of all additives at 304SS

### 3.1.2- Effect of Temperature

The corrosion of stainless steel type 304 in 1 M HCl in absence and presence of different concentrations of the used inhibitors (ca.  $1.0 \times 10^{-6}$  to  $5 \times 10^{-4}$  M) at temperatures range ( $25\text{--}55^{\circ}\text{C}$ ) was studied using weight loss method. The inhibition efficiency at

different temperatures is tabulated in Table 2. Fig.5 shows the plot of the inhibition efficiency against logarithm of concentration of inhibitor ( $C$ ) at different temperatures. The data reveal that the extent of inhibition efficiency increases with the concentration of the inhibitors and decreases with increasing temperature.

Table 2 - The effect of temperature on the inhibition efficiency of SS type 304 in 1 M HCl containing different concentrations of the inhibitors.

Temperature T (°C)	Concentration (M inhibitor)	A		B		C	
		□	%IE	□	%IE	□	%IE
25°C	1x10 <sup>-6</sup>	0.238	23.8	0.366	36.6	0.405	40.5
	5x10 <sup>-6</sup>	0.554	55.4	0.614	61.4	0.715	71.5
	1x10 <sup>-5</sup>	0.670	67.0	0.750	75.0	0.770	77.0
	5x10 <sup>-5</sup>	0.777	77.7	0.796	79.6	0.888	88.8
	1x10 <sup>-4</sup>	0.803	80.3	0.845	84.5	0.907	90.7
	5x10 <sup>-4</sup>	0.879	87.9	0.866	86.6	0.932	93.2
35°C	5x10 <sup>-6</sup>	0.533	53.3	0.566	56.6	0.686	68.6
	1x10 <sup>-5</sup>	0.590	59.0	0.705	70.5	0.751	75.1
	5x10 <sup>-5</sup>	0.763	76.3	0.774	77.4	0.869	86.9
	1x10 <sup>-4</sup>	0.781	78.1	0.793	79.3	0.889	88.9
	5x10 <sup>-4</sup>	0.878	87.8	0.869	86.9	0.935	93.5
45°C	5x10 <sup>-6</sup>	0.352	35.2	0.399	39.9	0.512	51.2
	1x10 <sup>-5</sup>	0.518	51.8	0.585	58.5	0.642	64.2
	5x10 <sup>-5</sup>	0.716	71.6	0.728	72.8	0.836	83.6
	1x10 <sup>-4</sup>	0.735	73.5	0.769	76.9	0.863	86.3
	5x10 <sup>-4</sup>	0.854	85.4	0.844	84.4	0.908	90.8
55°C	5x10 <sup>-6</sup>	0.287	28.7	0.330	33.0	0.293	29.3
	1x10 <sup>-5</sup>	0.425	42.5	0.467	46.7	0.443	44.3
	5x10 <sup>-5</sup>	0.667	66.7	0.680	68.0	0.762	76.2
	1x10 <sup>-4</sup>	0.687	68.7	0.729	72.9	0.834	83.4
	5x10 <sup>-4</sup>	0.835	83.5	0.826	82.6	0.899	89.9

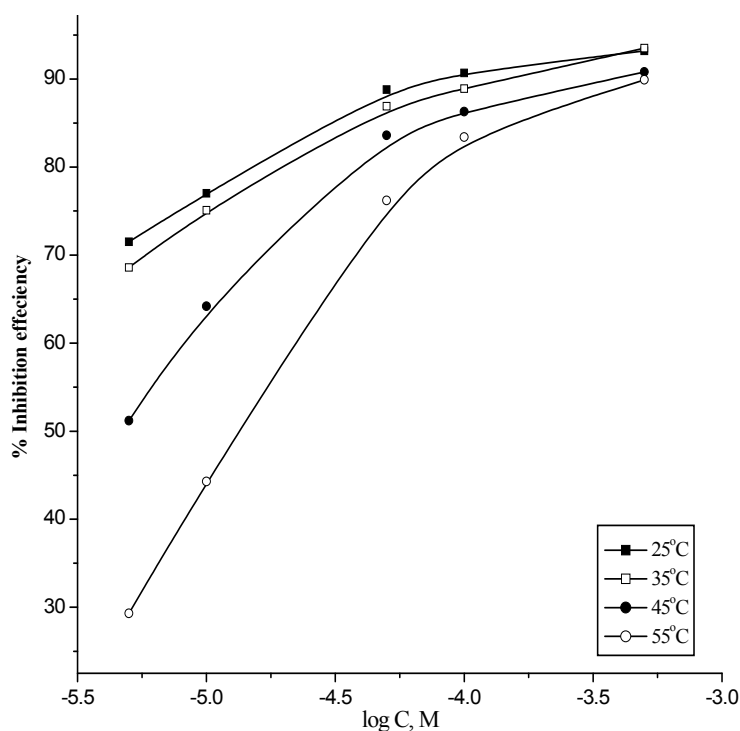


Fig. 5 – Inhibition efficiency for different concentrations of compound (C) at sifferent temperatures

The activation energy of the corrosion process can be calculated using Arrhenius-type equation:

$$k = A \exp(-E_a^*/RT) \quad (4)$$

where  $k$  is the corrosion rate,  $A$  is the frequency factor,  $E_a^*$  is the activation energy,  $R$  is the universal gas constant and  $T$  is the absolute temperature.

Plotting  $\log k$  vs.  $1/T$  for SS type 304 in 1 M HCl in the absence and presence of  $5 \times 10^{-5}$  M from the investigated inhibitors is shown in Fig. 5. As shown from this Figure, straight lines were obtained, the values of  $E_a^*$  can be calculated from the slopes of the straight lines. The value of  $E_a^*$  obtained in 1 M HCl is equal to  $44.32 \text{ kJ mol}^{-1}$ . The energy of activation for the compounds studied are listed in Table 3. The activation energy is higher in the presence of additives than in their absence. These types of inhibitors retard the corrosion process at ordinary temperature [8] whereas the inhibition is considerably decreased at elevated temperature. The higher values of  $E_a^*$  are good evidence for the strong adsorption of 3-thiazinonyl-bicyclo[4.2.0] octene-carboxylate derivatives on the steel surface.

Table 3 - Activation energy for corrosion of SS type 304 in 1 M HCl in absence and presence of  $5 \times 10^{-5}$  M of the additives

Compound	$E_a^*$ , $\text{kJ mol}^{-1}$
1M HCl	44.32
A	55.23
B	56.60
C	64.00

Free energies of activation ( $\Delta G^*$ ) were calculated by applying the transition state equation [9]:

$$\Delta G^* = RT \left[ \ln \frac{KT}{h} - \ln(\text{corrosionrate}) \right] \quad (5)$$

where,  $h$  is Planck's constant,  $K$  is Boltzman's constant,  $R$  is gas constant and  $T$  is absolute temperature. The enthalpy of activation ( $\Delta H^*$ ) and the entropy of activation ( $\Delta S^*$ ) were calculated by applying the following equations [10]:

$$\Delta H^* = E_a^* - RT \quad (6)$$

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \quad (7)$$

Table 4 - Thermodynamic activation parameters  $\Delta G^*$ ,  $\Delta H^*$  &  $\Delta S^*$  of SS type 304 dissolution in 1 M HCl at different temperatures.

Inhibitors used	Thermodynamic activation parameters	Temperature, °C			
		25	35	45	55
1M HCl	$\Delta G^*$ ( $\text{kJ mol}^{-1}$ )	85.70	87.09	88.79	89.95
	$\Delta H^*$ ( $\text{kJ mol}^{-1}$ )	41.84	41.76	41.68	41.59
	$-\Delta S^*$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	147.2	147.2	148.1	147.4
A	$\Delta G^*$ ( $\text{kJ mol}^{-1}$ )	89.42	90.78	92.13	92.95
	$\Delta H^*$ ( $\text{kJ mol}^{-1}$ )	52.75	52.67	52.59	52.50
	$-\Delta S^*$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	123.1	123.7	124.3	123.3
B	$\Delta G^*$ ( $\text{kJ mol}^{-1}$ )	89.65	90.90	92.23	93.06
	$\Delta H^*$ ( $\text{kJ mol}^{-1}$ )	54.12	54.04	53.96	53.87
	$-\Delta S^*$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	119.2	119.7	120.3	119.5
C	$\Delta G^*$ ( $\text{kJ mol}^{-1}$ )	91.13	92.30	93.57	93.87
	$\Delta H^*$ ( $\text{kJ mol}^{-1}$ )	61.52	61.44	61.36	61.27
	$-\Delta S^*$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )	99.4	100.2	101.3	99.4

The values of the thermodynamic parameter for the dissolution of SS type 304 in 1 M HCl are listed in Table 6. Inspection of these data reveal that the values of ( $\Delta H^*$ ) and ( $\Delta G^*$ ) in the presence of 3-thiazinonyl-bicyclo[4.2.0]octene-carboxylate derivatives increase over that of the uninhibited solution. This implies that energy barrier of the corrosion reaction in the presence of 3-thiazinonyl-bicyclo[4.2.0] octene-carboxylate derivatives increases. On the other hand ( $\Delta S^*$ ) values are lower and have negative values in presence of 3-thiazinonyl-bicyclo[4.2.0] octene-carboxylate derivatives. This means that addition of these compounds cause a decrease in the disordering in going from reactants to the activated complexes [11, 12]. Also, from Table 6, it is evident that the values of ( $\Delta G^*$ ) increase with increasing temperature where the constantly values of ( $\Delta H^*$ ) indicated that the mechanism of the corrosion reaction was not changed by raising the temperatures from  $25^\circ\text{C}$  to  $55^\circ\text{C}$ .

Table 5 - Shows the effect of inhibitors concentrations on the corrosion kinetics parameters such as anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ),  $E_{corr}$ ,  $I_{corr}$ ,  $R_p$ ,  $\theta$  and %IE.

Inh.	Inhibitor Conc.,M	$-E_{corr}$ (mV)	$I_{corr}$ ( $\mu\text{A cm}^{-2}$ )	$-\beta_c$ (mV dec $^{-1}$ )	$\beta_a$ (mV dec $^{-1}$ )	$R_p \times 10^{-2}$ (Ohm $\text{cm}^2$ )	$\theta$	% IE
A	1 M HCl	452.3	269.9	125.5	79.4	78.27	----	----
	$1 \times 10^{-6}$	446.3	193.5	121.4	82.3	1.10	0.283	28.3
	$5 \times 10^{-6}$	427.0	104.5	117.5	68.1	1.79	0.613	61.3
	$1 \times 10^{-5}$	422.6	81.1	115.1	63.1	2.18	0.700	70.0
	$5 \times 10^{-5}$	392.0	44.9	114.4	53.1	3.51	0.834	83.4
	$1 \times 10^{-4}$	377.4	20.9	107.2	47.6	6.85	0.923	92.3
	$5 \times 10^{-4}$	369.5	18.9	106.7	46.2	7.42	0.930	93.0
B	$1 \times 10^{-6}$	436.0	115.9	117.7	76.7	1.74	0.571	57.1
	$5 \times 10^{-6}$	418.8	61.5	113.3	68.5	3.02	0.772	77.2
	$1 \times 10^{-5}$	414.2	51.4	110.0	62.5	3.37	0.810	81.0
	$5 \times 10^{-5}$	391.5	38.6	107.0	58.7	4.26	0.857	85.7
	$1 \times 10^{-4}$	370.8	23.0	114.5	50.3	6.60	0.915	91.5
	$5 \times 10^{-4}$	363.7	19.3	113.6	46.8	7.48	0.929	92.9
C	$1 \times 10^{-6}$	424.8	83.2	121.4	76.8	2.37	0.692	69.2
	$5 \times 10^{-6}$	401.8	49.0	113.5	57.5	3.38	0.818	81.8
	$1 \times 10^{-5}$	392.6	25.5	115.1	44.9	5.30	0.905	90.5
	$5 \times 10^{-5}$	369.5	18.4	114.4	43.7	7.36	0.932	93.2
	$1 \times 10^{-4}$	354.6	15.1	107.2	46.1	9.58	0.944	94.4
	$5 \times 10^{-4}$	338.1	12.6	106.7	49.4	1.23	0.953	95.3

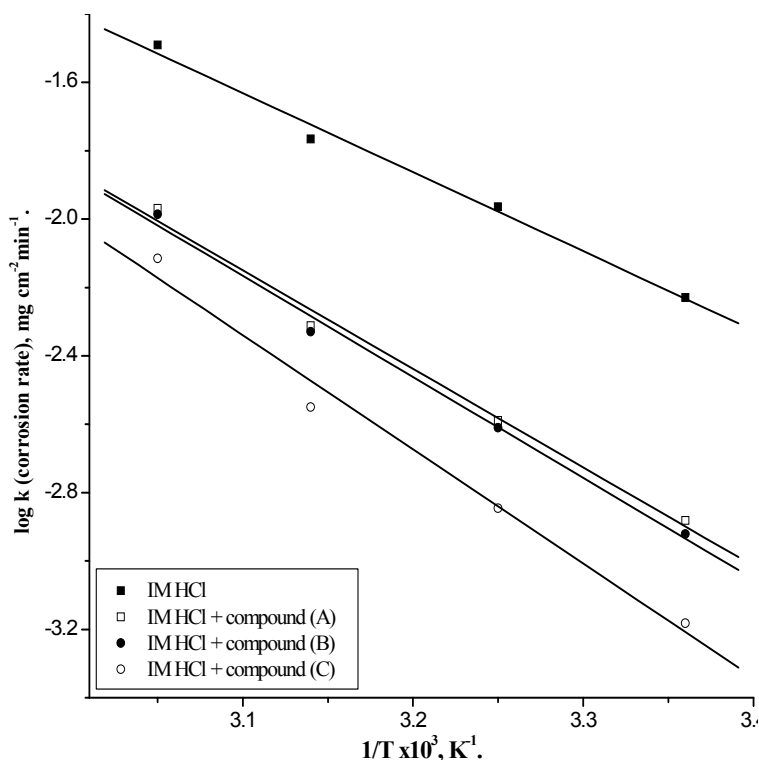


Fig. 6 –  $\log k$  vs  $1/T$  for SS type 304 in 1 M HCl in absence and presence of  $5 \times 10^{-5}$  M the additives

### 3.2. Potentiodynamic Polarization measurements

Addition of different concentrations of the used inhibitors on the anodic and cathodic polarization of 304SS was studied in 1.0 M HCl. Fig. 7 shows that

the effect of the used inhibitors on anodic and cathodic polarization. The degree of surface coverage,  $\theta$  at constant potential is given by the following relation [13,14]:

$$\theta = 1 - I_{corr\ add} / I_{corr\ free} \quad (8)$$

where  $I_{corr\ free}$  and  $I_{corr\ add}$  are the corrosion currents of uninhibited and inhibited experiments, respectively.

The %IE at each concentration was calculated using the equation:

$$\%IE = (1 - I_{corr\ add} / I_{corr\ free}) \times 100 \quad (9)$$

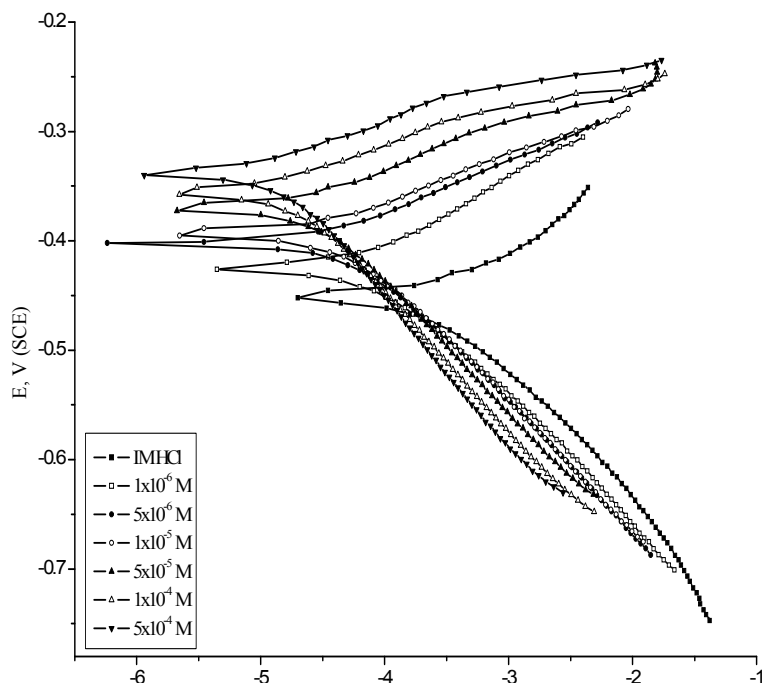


Fig. 7 – potentiodynamic polarization curves for the corrosion of SS type 304 in 1M HCl in absence and presence of different concentrations of inhibitor (C) at 25°C at 5 mV/S

An inspection of the results obtained from Table 6 reveals that, the increasing in the concentration of the additive compounds shows the following:

(i) Tafel slopes indicating anodic effect on the corrosion mechanism.

(ii) The corresponding values of  $\beta_a$  showed a similar trend as those for  $\beta_c$ , the relatively lower values found in this study for the stainless steel compared to those found for mild steel [15] and iron [16], are due to less impurities present in stainless steel.

(iii) The corrosion potential ( $E_{corr}$ ) shifted to more positive values while the corrosion current densities decrease with increasing the inhibitor concentration indicates the inhibiting effect of these compounds.

(iv) The %IE calculated from weight loss and polarization measurements was found to increase with increasing the inhibitor concentration. The inhibition achieved by these compounds decreases in the following order:

Compound C > Compound B > Compound A

It is interest to note that, the values of IE given by polarization are higher than those obtained by weight

loss measurements. These results may be due to the fact that, the electrochemical measurements were carried out on freshly prepared solutions.

The inhibiting effect of these compounds can be attributed to their parallel adsorption at the metal solution interface. The parallel adsorption is owing to the presence of one or more active center for adsorption. The chemisorption takes place by the formation of a chemical bond between the metal and the adsorbed molecule. Chemisorption involves charge or charge transfer from inhibitor molecule to the metal surface forming co-ordinate type bond [17].

#### 4. CONCLUSIONS

3- thiazinonyl-bicyclo [4.2.0] octene-carboxylate derivatives drugs have proved to be efficient inhibitors for corrosion of SS type 304 in 1 M HCl solution. These inhibitors act as anodic type inhibitors and IE was found to increase by increasing the inhibitor concentration and decreasing of temperature. The %IE obtained from polarization measurements show good agreement with those obtained from weight loss experiments.

The inhibition of SS type 304 in 1 M HCl solution was found to obey Langmuir adsorption



isotherm. The thermodynamic values obtained from this study  $E_a$ ,  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  indicate that the presence of the inhibitors increases the activation energy and the negative values of  $\Delta G$  indicate spontaneous adsorption of the inhibitor on the surface of the steel.

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