



Inhibition of Carbon steel corrosion in Hydrochloric Acid solutions by benzothiazol Derivatives

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Abstract: The inhibiting effect of inhibitor A; 2-(benzo [d] thiazol-2-yl)-3-(4-nitrophenyl) acrylonitrile and inhibitor B; 2-(benzo [d] Thiazol-2-yl) acetonitrile on the corrosion of carbon steel (C-steel) in 1M HCl was studied by weight loss technique at different temperatures, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques at 30°C. The inhibition efficiency (I.E. %), and the coverage surface area of C-steel (Θ) by each inhibitor of different concentrations were calculated by weight loss and EIS techniques. I.E. % depended on the concentrations and type of investigated inhibitors. I.E.% decreased with rise temperatures, this corresponded to the surface coverage by inhibitors. The results showed that the inhibitors were adsorbed on C-steel surface according to Langmuir (inhibitor A) and Temkin (inhibitor B) adsorption isotherm. The values of standard free energy of adsorption ($\Delta G^{\circ}_{ads.}$), the enthalpy change of adsorption ($\Delta H^{\circ}_{ads.}$), and the values of entropy change of adsorption ($\Delta S^{\circ}_{ads.}$), for each inhibitor were calculated at all studied temperatures. The activation energy (E^*_a), the enthalpy change of activation (ΔH^*), and the entropy change of activation (ΔS^*), of C-steel corrosion were calculated in 1M HCl with absence and presence different concentrations of investigated inhibitors. The fraction of over-voltage assisting the dissolution of C-steel anode (α_a), were calculated in absence and presence the used inhibitors of different concentrations in 1M HCl.

[F. A. Ali, A. S Fouda, A. S. M. Diab, T. O. Habib. **Inhibition of Carbon steel corrosion in Hydrochloric Acid solutions by benzothiazol Derivatives.** *N Y Sci J* 2020;13(4):9-19]. ISSN 1554-0200 (print); ISSN 2375-723X (online). <http://www.sciencepub.net/newyork>. 2. doi: [10.7537/marsnys130420.02](https://doi.org/10.7537/marsnys130420.02).

Keywords: Corrosion; Thiazoles derivatives; C-steel; Hydrochloric acid; Langmuir adsorption isotherm; Temkin's adsorption isotherm; impedance (EIS).

1. Introduction:

Corrosion of metals has been a persisting problem in society and, hence, it is an important area of research. Corrosion protection is often afforded by isolating metals from the corrosive environment using inhibitors Hydrochloric acid is generally used for the removal of undesirable scale and rust in several industrial process. Thus, Inhibitors are one of the most convenient methods for protection against corrosion, particularly in acid solutions to prevent unexpected metal dissolution and acid consumption⁽¹⁻³⁾.

Corrosion of mild steel and its inhibition in acidic solutions have attracted the attention of a number of investigations⁽⁴⁻⁷⁾.

The protection of metal against corrosion can be achieved by adding a small concentration of organic compounds to the environment⁽⁸⁾. A variety of organic compounds containing heteroatoms like nitrogen, sulfur, and oxygen have been investigated as corrosion inhibitors⁽⁹⁾. A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time such as compounds including triazole derivatives⁽¹⁰⁾.

2. Experimental

Materials and Reagents

The working electrode was mechanically cut from C-steel to prepared samples in the form of sheets [having composition (weight %) C 0.2; Mn 0.9; P0.007; Si 0.002% and the rest Fe].

The surface of each sample was abraded using different grades (up to 1200 grade) of emery papers, degreased with acetone, washed with bidistilled water and dried with soft paper. The experimental measurements were carried out in 1M HCl solution in the absence and presence of various concentrations of inhibitors A and B for all studies. The name, chemical structure, molecular weight and molecular formulae of the inhibitors A and B are given in Table 1. The concentrations of inhibitors employed were varied from $5 \times 10^{-6} \text{M}$ to $21 \times 10^{-6} \text{M}$ for each experiment, a freshly prepared solution was used.

Weight loss method

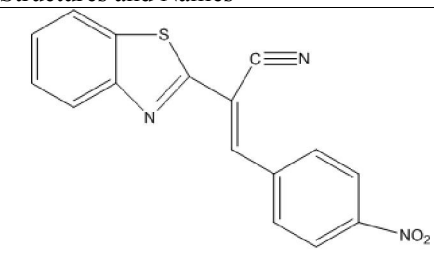
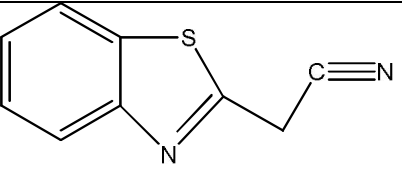
Three parallel C- steel sheets of 2X2X0.2 cm were abraded with emery paper up to 1200 grit, washed with bidistilled water and acetone. After weighting accurately, the sheets were immersed in 100 ml beaker, which contained 100ml 1M HCl with and

without addition of different concentrations of inhibitors at $25 \pm 1^\circ\text{C}$. The test sheets were suspended by suitable glass hooks at the edge of the basin, and under the surface of the test solution by about 1 cm. All the aggressive acid solutions were open to air. After specified immersion time equals 120 min., the sheets were taken out, washed, dried, and weighed. The average weight loss of the three parallel C-steel sheets at a certain time (120 min.) was taken in mg cm^{-2} at the temperature of 303°K , 308°K , 313°K and 318°K in water thermostat. The change in weight was recorded to the nearest 0.0001 g. Precautions were always made to avoid scratching the sheet during washing after exposure. Therefore, the value of weight

loss equals $w_1 - w_2 = \Delta w'$ of each sheet, and by divided $\Delta w'$ on the exposure surface area of the sheet (a), it

gives $\frac{\Delta w'}{cm^2}$ (Δw). So, we can calculate later in discussion, the values of $(C.R)_{inh.}$ and $(C.R)_{free.}$ to calculate the values of coverage surface area of C-steel (Θ) and I.E.% of investigated of inhibitors. Where w_1 and w_2 are the weights of sheets before and after reaction, respectively and a is the surface area of each sheet in cm^2 . Also $(C.R)_{inh.}$ and $(C.R)_{free.}$ are the corrosion rate of C-steel in 1M HCl with presence and absence the investigated inhibitors respectively.

Table 1: The name, chemical structure, molecular weight and molecular formulae of the inhibitors A and B:-

Inhibitor	Structures and Names	Mol. Wt., Mol. Formulas
A	 <i>(E)</i> -2-(benzo[d]thiazol-2-yl)-3-(4-nitrophenyl)acrylonitrile	308.91g C ₁₆ H ₉ N ₃ O ₂ S
B	 2-(benzo[d]thiazol-2-yl)acetonitrile	175.1108 g C ₉ H ₆ N ₂ S

Potentiodynamic polarization measurements

Polarization experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (1cm^2) and a saturated calomel electrode (SCE) coupled to a fine luggin capillary as the reference electrode. The working electrode was in the form of square cut from C-steel sheet ($1 \times 1\text{ cm}$) embedded in epoxy resin of polytetrafluoroethylene, so the flate surface was the only surface in the electrode. Before polarization scanning, working electrode was immersed in the test electrolyte of 100 ml in volume for 30 min. until steady state and the open circuit potential (OCP) was attained which was taken as E_{oc} . All experiments were carried out at $30 \pm 1^\circ\text{C}$ using lab companion circulator thermostat and solution were not deaerated.

For potentiodynamic polarization measurements, the potential was scanned at scan rate of 1 mV s^{-1} . Potential changed automatically from -1000mv up to

+300 mV_{SCE} . The values of α_a (fraction of overvoltage which assist the dissolution of C-steel at anode) in 1M HCl with absence and presence different concentrations of used inhibitors at 30°C can evaluate in discussion from slope of Tafel equation.

4-Electrochemical impedance spectroscopy (EIS) measurements

The EIS spectra were recorded at open circuit potential (OCP) after immersion the electrode for 30 min. in test solution. The AC signal was 5 mV peak to peak and the frequency range studied was between 100 kHz and 0.2 Hz. I.E. % and Θ of the used inhibitors can obtained in discussion from impedance measurements.

Results and Discussion

A-Chemical technique (weight loss technique):-

Figure (1) and others not shown display a relation between the weight loss (mg cm^{-2}); Δw , vss.

time (min.), for the reaction of (C-steel) of definite surface area in of 1M HCl solution in absence and presence of different concentrations of the used inhibitors A and B at different temperatures. It is essential to note that (C.R.) of the reaction of C-steel with 1M HCl in presence of the used inhibitors

$\left(\frac{\Delta W}{\partial t}\right)_{inh.}$ decreases than with 1M HCl only. This due to adsorption of inhibitors A and B on C-steel surface retard the attack of HCl molecules with C-steel. (C.R.)_{inh.} of C-steel also decreases with increasing the concentrations of each inhibitor from (5-21)X10⁻⁶M. This case was simply related to Θ of C-steel by adsorbant (inhibitors) increases to protect C-steel from corrosion.

It is essential to note also from the figures that C.R. of C-steel and I.E.% of the same concentrations of each inhibitor in 1M HCl increases and decreases respectively with increasing the temperature of the reaction.

This indicate that the behavior of both inhibitors on C-steel surface occur through physi-sorption type (11).

The C.R. of C-steel in 1M HCl with absence

(C.R.)_{free;} $\left(\frac{\Delta W_{free.}}{\partial t}\right)$, and presence (C.R.)_{inh.}, $\left(\frac{\Delta W_{inh.}}{\partial t}\right)$ of the used inhibitors, were calculated from Figure (1) and others not shown and hence were listed in tables (1-8).

Table (1): Weight loss measurements, corrosion rate, coverage surface area (Θ), and inhibition efficiency (%I.E.) for corrosion of carbon steel in 1M HCl with absence and presence different concentrations of inhibitor A after 120 minutes at 30°C.

Concentration [M]	Weight loss (mg cm ⁻²)	Corrosion rate (mg cm ⁻² min ⁻¹)	θ	I.E.%
Blank	6.252	0.0521	-	-
5x10 ⁻⁶	2.256972	0.0188031	0.639	63.9
9x10 ⁻⁶	2.050656	0.0170888	0.672	67.2
13x10 ⁻⁶	1.756812	0.0146401	0.719	71.9
17x10 ⁻⁶	1.34418	0.0112015	0.785	78.5
21x10 ⁻⁶	0.981564	0.0081797	0.843	84.3

Table (2): Weight loss measurements, corrosion rate, coverage surface area (Θ), and inhibition efficiency (%I.E.) for corrosion of carbon steel in 1M HCl with absence and presence different concentrations of inhibitor A after 120 minutes at 35°C.

Concentration [M]	Weight loss (mg cm ⁻²)	Corrosion rate (mg cm ⁻² min ⁻¹)	θ	IE%
Blank	6.768	0.0564	-	-
5x10 ⁻⁶	2.517696	0.0209808	0.628	62.8
9x10 ⁻⁶	2.30112	0.019176	0.66	66.0
13x10 ⁻⁶	1.935648	0.0161304	0.714	71.4
17x10 ⁻⁶	1.62432	0.013536	0.76	76.0
21x10 ⁻⁶	1.123488	0.0093624	0.834	83.4

Table (3): Weight loss measurements, corrosion rate, coverage surface area (Θ), and inhibition efficiency (%I.E.) for corrosion of carbon steel in 1M HCl with absence and presence different concentrations of inhibitor A after 120 minutes at 40°C.

Concentration [M]	Weight loss (mg cm ⁻²)	Corrosion rate (mg cm ⁻² min ⁻¹)	θ	IE%
Blank	7.32	0.061	-	-
5x10 ⁻⁶	2.99388	0.024945	0.591	59.1
9x10 ⁻⁶	2.75964	0.022997	0.623	62.3
13x10 ⁻⁶	2.4156	0.02013	0.67	67.0
17x10 ⁻⁶	1.96176	0.016348	0.732	73.2
21x10 ⁻⁶	1.48596	0.012383	0.797	79.7

Table (4): Weight loss measurements, corrosion rate, coverage surface area (Θ), and inhibition efficiency (%I.E.) for corrosion of carbon steel in 1M HCl with absence and presence different concentrations of inhibitor A after 120 minutes at 45°C.

Concentration [M]	Weight loss (mg cm ⁻²)	Corrosion rate (mg cm ⁻² min ⁻¹)	θ	IE%
Blank	8.16	0.068	-	-
5x10 ⁻⁶	3.57408	0.029784	0.562	56.2
9x10 ⁻⁶	3.31296	0.027608	0.594	59.4
13x10 ⁻⁶	2.87232	0.023936	0.648	64.8
17x10 ⁻⁶	2.31744	0.019312	0.716	71.6
21x10 ⁻⁶	1.81968	0.015164	0.777	77.7

Table (5): Weight loss measurements, corrosion rate, coverage surface area (Θ), and inhibition efficiency (%I.E.) for corrosion of carbon steel in 1M HCl with absence and presence different concentrations of inhibitor B after 120 minutes at 30°C.

Concentration [M]	Weight loss (mg cm ⁻²)	Corrosion rate (mg cm ⁻² min ⁻¹)	θ	IE%
Blank	6.252	0.0521	-	-
5x10 ⁻⁶	2.819652	0.0234971	0.549	54.9
9x10 ⁻⁶	2.588328	0.0215694	0.586	58.6
13x10 ⁻⁶	2.113176	0.0176098	0.662	66.2
17x10 ⁻⁶	1.956876	0.0163073	0.687	68.7
21x10 ⁻⁶	1.600512	0.0133376	0.744	74.4

Table (6): Weight loss measurements, corrosion rate, coverage surface area (Θ), and inhibition efficiency (%I.E.) for corrosion of carbon steel in 1M HCl with absence and presence different concentrations of inhibitor B after 120 minutes at 35°C.

Concentration [M]	Weight loss (mg cm ⁻²)	Corrosion rate (mg cm ⁻² min ⁻¹)	θ	IE%
Blank	6.768	0.0564	-	-
5x10 ⁻⁶	3.343392	0.0278616	0.506	50.6
9x10 ⁻⁶	3.01176	0.025098	0.555	55.5
13x10 ⁻⁶	2.612448	0.0217704	0.614	61.4
17x10 ⁻⁶	2.321424	0.0193452	0.657	65.7
21x10 ⁻⁶	2.016864	0.0168072	0.702	70.2

Table (7): Weight loss measurements, corrosion rate, coverage surface area (Θ), and Inhibition efficiency (%I.E.) for corrosion of carbon steel in 1M HCl with absence and presence different concentrations of inhibitor B after 120 minutes at 40°C.

Concentration [M]	Weight loss (mg cm ⁻²)	Corrosion rate (mg cm ⁻² min ⁻¹)	θ	IE%
Blank	7.32	0.061	-	-
5x10 ⁻⁶	4.64088	0.038674	0.366	36.6
9x10 ⁻⁶	4.17972	0.034831	0.429	42.9
13x10 ⁻⁶	3.71856	0.030988	0.492	49.2
17x10 ⁻⁶	3.2208	0.02684	0.560	56.0
21x10 ⁻⁶	2.82552	0.023546	0.614	61.4

Table (8): Weight loss measurements, corrosion rate, coverage surface area (Θ), and Inhibition efficiency (%I.E.) for corrosion of carbon steel in 1M HCl with absence and presence different concentrations of inhibitor B after 120 minutes at 45°C.

Concentration [M]	Weight loss (mg.cm ⁻²)	Corrosion rate (mg.cm ⁻² .min ⁻¹)	θ	%I.E
Blank	8.16	0.068	-	-
5x10 ⁻⁶	5.64672	0.047056	0.308	30.8
9x10 ⁻⁶	5.29584	0.044132	0.351	35.1
13x10 ⁻⁶	4.90416	0.040868	0.399	39.9
17x10 ⁻⁶	4.29216	0.035768	0.474	47.4
21x10 ⁻⁶	4.04736	0.033728	0.504	50.4

I.E.%, and Θ of C-steel by each inhibitor of different concentrations at different temperatures were calculated by using the following relations respectively. ^(12,13)

$$\text{I.E. \%} = \left(1 - \frac{(C.R)_{inh.}}{(C.R)_{free.}}\right) \times 100 \quad \text{-----(1)}$$

$$\Theta = 1 - \frac{(C.R)_{inh.}}{(C.R)_{free.}} \quad \text{-----(2)}$$

The values of I.E. %, Θ were listed also in tables (1-8). The values of I.E.% of inhibitor A are major than inhibitor B at all concentrations and different temperatures. The values of Θ of C-steel by inhibitors A and B of different concentrations in 1M HCl solution at different temperatures could fit, Langmuir and Temkin adsorption isotherm respectively ⁽¹³⁻¹⁵⁾;

$$\frac{C_{inh.}}{\theta} = \frac{1}{K_{ads}} + C_{inh.} \quad \text{-----(3)}$$

$$\theta = \left(\frac{2.303}{a}\right) \text{Log} K_{ads} + \frac{2.303}{a} \text{Log} C_{inh.} \quad \text{-----(4)}$$

Where $K_{ads.}$ is the equilibrium constant of the adsorption process; is the strength for the adsorption force between inhibitor molecules and the metal surface, $C_{inh.}$ is the inhibitor concentration, Θ is the coverage surface area of C-steel by each inhibitor at definite concentration and temperature.

Figures (2,3) offer a relation of $\frac{C_{inh.}}{\theta}$ vss. $C_{inh.}$ and Θ vss. $\text{Log } C_{inh.}$ at different temperatures, to calculate the values of $K_{ads.}$ of inhibitors A and B from

intercept

the intercept and slope respectively.

A-1- Thermodynamic adsorption parameters:-

The values of standard free energy of adsorption of each inhibitor ($\Delta G_{ads.}^{\circ}$, in Kj mole^{-1}), on the C-steel surface in 1M HCl at all studied temperatures can be calculated by the following equation. ⁽¹⁶⁻¹⁸⁾

$$K_{ads.} = \frac{1}{55.5} e^{\frac{-\Delta G_{ads.}^{\circ}}{RT}} \quad \text{-----(5)}$$

Where 55.5 is the concentration of water in (M) at metal /solution interface.

The heat of adsorption ($\Delta H_{ads.}^{\circ}$) could be calculated according to the Van't Hoff equation; ^(19,20)

$$\text{Log} K_{ads.} = \left(\frac{-\Delta H_{ads.}^{\circ}}{2.303R}\right) \frac{1}{T} + \text{constant} \quad \text{-----(6)}$$

In order to calculate enthalpy of adsorption ($\Delta H_{ads.}^{\circ}$), $\log K_{ads.}$ was plotted against $\frac{1}{T}$ as shown in

figure (4) of inhibitor A and other not shown of inhibitor B. The straight line was obtained with slope

equal to $\left(\frac{-\Delta H_{ads.}^{\circ}}{2.303R}\right)$. Then in accordance with Gibb's equation. ⁽²¹⁾

$$\Delta G_{ads.}^{\circ} = \Delta H_{ads.}^{\circ} - T\Delta S_{ads.} \quad \text{-----(7)}$$

By introducing the obtained $\Delta G_{ads.}^{\circ}$ and $\Delta H_{ads.}^{\circ}$ values in equation (7), the values of entropy change of adsorption inhibitors molecules ($\Delta S_{ads.}$) were calculated at all studied temperatures.

All estimated thermodynamic adsorption parameters for the studied inhibitors on C-steel in 1M HCl solution were listed in tables (9,11). Inspection of the obtained data, it was found that; $\Delta G_{ads.}^{\circ}$ Values of the used inhibitors at different temperatures are negative sign. This indicate that the adsorption of the used inhibitors on C-steel surface are spontaneous process. ^(19, 21-23)

The negative $\Delta G_{ads.}$ values of inhibitor A are major than inhibitor B at the same concentrations and temperatures. This means that the physi-sorption forces between inhibitor A molecules (adsorbant) and steel surface (adsorbent) are major than in case of inhibitor B.

It is usually accepted that the values of $\Delta G_{ads.}^{\circ}$ of the used inhibitor vary between 14.79Kj mole^{-1} to 39.99Kj mole^{-1} . This case was simply confirm to us that adsorption process of the used inhibitors on C-steel surface in the test aggressive medium is through physisorption type ⁽¹¹⁾

The negative sign of $\Delta H_{ads.}^{\circ}$ reveals that the adsorption of inhibitor molecules is an exothermic process. Generally an exothermic adsorption process suggests either physi-sorption or chemisorption while endothermic process is attributed to chemisorption. ⁽²⁴⁾

Generally, enthalpy values up to 41.9Kj mole^{-1} are related to physi-sorption while those around 100Kj mole^{-1} or higher are attributed to chemisorption. ^(25,26)

In case of investigated inhibitors, the values of enthalpy are relatively low, approaching those typical of physi-sorption.

The values of $\Delta S_{ads.}^{\circ}$ in the presence of investigated inhibitors are negative that is accompanied with exothermic adsorption process ⁽²⁷⁾. It is clear also from tables (9,11) that the values of $\Delta S_{ads.}^{\circ}$ and $\Delta H_{ads.}^{\circ}$; at the same concentrations and temperatures of the used inhibitors, of inhibitor A lower and major than inhibitor B respectively.

This case confirms to us that the coverage surface area (Θ) and the number of adsorbed inhibitor molecules on C-steel surface in presence of inhibitor A are larger and lower than in presence of inhibitor B respectively. In the other word, this means that the molecules of inhibitors (1) and (2) adsorbed

horizontality and verticality on the surface of adsorbent (C-steel) respectively.

Table (9): Thermodynamic adsorption parameters for inhibitor (1); were calculated from Langmuir adsorption isotherm, on carbon steel surface in 1M HCl at different temperatures.

Temp°C	$K_{ads} \times 10^4$ M ⁻¹	$-\Delta G_{ads}^{\circ}$ kJ mol ⁻¹	$-\Delta H_{ads}^{\circ}$ KJ mol ⁻¹	ΔS_{ads}° J mol ⁻¹ K ⁻¹
30	13.49	39.90	42.1	7.26
35	12.59	40.38	42.1	5.58
40	7.94	39.84	42.1	7.22
45	6.61	39.99	42.1	6.64

Table (10): Activation parameters for carbon steel corrosion with absence and presence of different concentrations of inhibitor A in 1M HCl.

Concentration of inhibitor (M)	E_a^* kJ mol ⁻¹	$-\Delta H^*$ KJ mol ⁻¹	ΔS^* -J mol ⁻¹ K ⁻¹
Blank	13.0	9.72	267.9
5X10 ⁻⁶	36.37	30.96	270.8
9X10 ⁻⁶	39.68	34.94	271.2
13X10 ⁻⁶	43.88	38.22	272.0
17X10 ⁻⁶	46.68	42.22	272.7
21X10 ⁻⁶	51.43	49.76	273.1

Table (11): Thermodynamic adsorption parameters for inhibitor B; were calculated from Temkin adsorption isotherm, on carbon steel surface in 1M HCl at different temperatures.

Temp°C	$K_{ads} \times 10^4$ M ⁻¹	$-\Delta G_{ads}^{\circ}$ kJ mol ⁻¹	$-\Delta H_{ads}^{\circ}$ KJ mol ⁻¹	$-\Delta S_{ads}^{\circ}$ J mol ⁻¹ K ⁻¹
30	6.36	14.79	9.15	18.61
35	5.92	14.85	9.15	18.51
40	5.53	14.91	9.15	18.40
45	5.38	15.08	9.15	18.65

A-2- Activation parameters of corrosion process:-

The activation energy E_a^* , the enthalpy change of activation ΔH^* , and the entropy change of activation ΔS^* , for the corrosion of C-steel in 1M HCl solution in absence and presence of different concentrations of investigated inhibitors were calculated from Arrhenius and transition-state equations respectively^(17,19).

The values of activation energy (E_a^*) were calculated by using the following Arrhenius equation^(17,28).

$$\text{Rate of corrosion } (k_{corr}) = A e^{\frac{-E_a^*}{RT}} \text{ -----(8)}$$

$$\text{Log}K_{corr.} = \text{Log}A - \left(\frac{E_a^*}{2.303R}\right) \times \frac{1}{T}$$

Where R is the general gas constant, T is the absolute temperature, and A is the Arrhenius constant depends on the sample type and electrolyte.

A plot of $K_{corr.}$ vs. $\frac{1}{T}$ as shown in figure (5) of inhibitor A and other not shown of inhibitor B. Straight lines were obtained with slope of each them

equals $\left(\frac{-E_a^*}{2.303R}\right)$ to calculate E_a^* of the reaction of C-steel with 1M HCl in each concentration of inhibitors A and B and listed in tables (10,12).

Table (12): Activation parameters for carbon steel corrosion with absence and presence of different concentrations of inhibitor B in 1M HCl.

Concentration of inhibitor (M)	E_a^* kJ mol ⁻¹	$-\Delta H^*$ KJ mol ⁻¹	ΔS^* -J mol ⁻¹ K ⁻¹
Blank	13.0	9.72	267.9
5X10 ⁻⁶	19.60	17.48	274.9
9X10 ⁻⁶	21.43	19.00	275.7
13X10 ⁻⁶	24.29	21.48	276.6
17X10 ⁻⁶	27.72	25.86	278.2
21X10 ⁻⁶	33.59	31.93	280.1

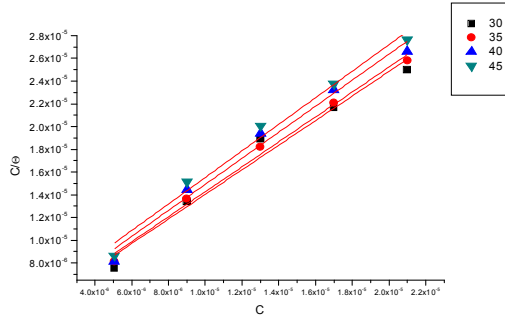


Figure (2): Langmuir adsorption isotherm [$C_{inh}, M/\theta$ vs. C_{inh}, M] of different concentrations of inhibitor A on carbon steel surface in 1 M HCl at different temperatures.

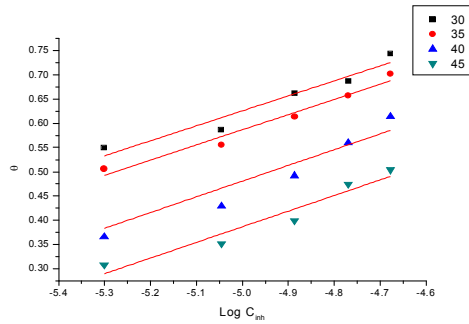


Figure (3): Temkin adsorption isotherm [θ vs. $\text{Log } C_{inh}, M$] of inhibitor B on carbon steel surface in 1 M HCl at different temperatures.

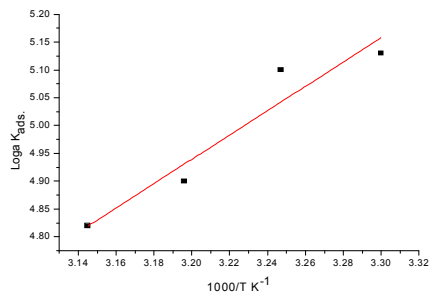


Figure (4): ($\text{Log } K_{ads}$) vs. ($1/T$) for the corrosion of carbon steel in 1M HCl with the presence of inhibitor A.

The enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) for the intermediate complex were obtained by applying the transition-state equation (25,29)

$$\text{Rate} (K_{corr}) = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \quad \text{-----(9)}$$

$$\text{Log} \left(\frac{K_{corr}}{T} \right) = \text{Log} \frac{R}{Nh} + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303R} \times \frac{1}{T}$$

Where K_{corr} is the corrosion rate, T is the absolute temperature, h is the Plank's constant and N is the Avogadro's number.

Figure (6) of inhibitor A and other not shown of

inhibitor B, represent $\left(\text{Log} \frac{K_{corr}}{T} \right)$ vs. $\frac{1}{T}$. Straight lines were obtained with slope and intercept of each

them equal $\left(\frac{-\Delta H^*}{2.303R} \right)$ and $\left[\text{Log} \frac{R}{Nh} + \frac{\Delta S^*}{2.303R} \right]$

respectively. The kinetic-thermodynamic parameters of ΔH^* and ΔS^* were calculated and listed in tables (10, 12). These tables clear that the values of E_a^* increase with increasing the concentrations of the used inhibitors. This case was simply related to the presence of these inhibitors induce an energy barrier for corrosion reaction and this barrier increases with increasing the concentrations of inhibitors.

The presence of investigated inhibitors render higher values of ΔH^* than these of inhibitors free solution.

The entropy change of activation (ΔS^*) has negative values. This indicates that the activated complex in slow step represents an association rather than dissociation. This meaning that, a decrease in disordering takes place on going from reactants to the activated complex (22,26)

B-Electrochemical techniques:-

B-1-Potentiodynamic polarization.

The all curves of polarization technique in figure (7) of inhibitor A and other figure not shown of inhibitor B display the variation of applied potentials [E, v (vs. SCE)] vs. $\text{Log } i, A \text{ cm}^{-2}$; for C-steel in absence and presence different concentrations of the used inhibitors in 1M HCl aqueous solution at 30°C, according to the following Tafel Equation: (30)

$$\zeta = \frac{-2.303RT}{\alpha F} \text{Log } i_0 + \frac{2.303RT}{\alpha F} \text{Log } i \quad \text{---(10)}$$

Where, ζ is the over-voltage; more positive and negative potential with respect to the free corrosion

potential (E_{corr}), $\frac{-2.303RT}{\alpha F} \text{Log } i_0$ is the intercept of $\frac{2.303RT}{\alpha F}$

Tafel line with the applied potential, $\frac{2.303RT}{\alpha F}$ is the anodic and cathodic Tafel slope depending on the polarization values with respect to E_{corr} .

The values of α_a ; the fraction of over-voltage assisting the dissolution of anode (C-steel), were evaluated from the linear portion slope of anodic Tafel curves of C-steel in absence and presence the used inhibitors of different concentrations in 1M HCl.

The calculated α_a values of the all Tafel curves were listed in Table (13).

Table (13): Effect of different concentrations of inhibitors A and B on Tafel Slope, and the fraction of over-voltage (α_a) which assisting the rate of dissolution at anode (carbon steel) in 1M HCl at 30 ° C.

Concentration of inhibitor in 1M HCl	Inhibitor 1		Inhibitor 2	
	Tafel Slope	α_a	Tafel Slope	α_a
Blank	0.066315018	0.91	0.066315018	0.91
5×10^{-6}	0.0738922	0.81	0.070608755	0.85
9×10^{-6}	0.082665288	0.73	0.077095424	0.78
13×10^{-6}	0.095680205	0.63	0.086970585	0.69
17×10^{-6}	0.12623353	0.48	0.1055459255	0.57
21×10^{-6}	0.187422472	0.32	0.1357042835	0.44

It is essential to note from table (13) that the values of α_a decrease with increasing the concentrations of both inhibitors A and B. This case is due to the higher concentration of inhibitors permits and improves of the inhibition efficiency of the inhibitors against C-steel corrosion by hindering the access of corrosive chloride ions to the steel substrates⁽³¹⁾, and hence suppress α_a values. On the other side, the values of α_a in the presence of inhibited C-steel were found to be lower than in blank. This due to presence of adsorbed layer of inhibitor isolates between corrosive environment and C-steel.

Table (13) clears also that, the values of α_a depend on the type of every inhibitor at the same concentrations. This does not depend only on the adsorption forces of each inhibitor with the surface of adsorbent (C-steel) but also due to the packing efficiency of inhibitors associated with the position of adsorbant molecules geometrically on the surface of C-steel; hence, we can say also that the inhibitor A and B adsorbed horizontally and vertically on the C-steel surface respectively.

B-2-Electrochemical impedance spectroscopy (EIS) measurements:-

The corrosion behavior of C- steel in 1M HCl solution in absence and presence different concentrations of inhibitors A and B was investigated by EIS technique at 30°C.

Figures (8, 9) display the Nyquist plots for C-steel in 1M HCl solution in absence and presence of different concentrations of inhibitors A and B at 30°C.

The impedance spectra of the different Nyquist plots in figures (8,9) was analyzed by fitting the experimental data to a simple equivalent Randles circuit model as given in figure (10), which includes the solution resistance (R_s) and the double layer capacitance (C_{dl}) which is placed in parallel to the charge transfer resistance (R_{ct})⁽³²⁾.

In 1M HCl with presence of various concentration of inhibitors A and B the impedance diagrams show the same trend (one capacitive loop), however, the diameter of this capacitive loop increases with increasing concentration of inhibitors.

The main parameters deduced from the analysis of Nyquist diagram are:

- 1- The resistance of charge transfer R_{ct}
- 2- The capacity of double layer C_{dl} which is define as;

$$C_{dl} = \frac{1}{2\pi F_{max} R_{ct}} \text{-----(11)}$$

Where F is the maximum frequency, the coverage surface area (Θ) and the inhibition efficiency obtained from impedance measurements are defined by the following relations;

$$\Theta = \left(1 - \frac{R_{ct}^{\circ}}{R_{ct}} \right) \text{-----(12)}$$

$$I.E. \% = \left(1 - \frac{R_{ct}^{\circ}}{R_{ct}} \right) \times 100 \text{-----(13)}$$

Where R_{ct}° and R_{ct} are the charge transfer resistance in absence and presence different concentrations of inhibitors respectively.

The impedance data such as C_{dl}, R_{ct}, Θ and I.E.% were estimated by assuming Randles circuit in figure (10) and are given in tables (14,15).

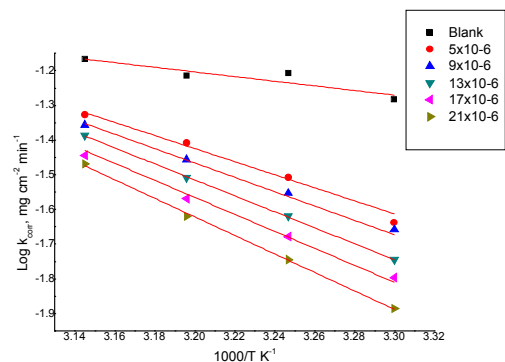


Figure (5): Arrhenius plots for carbon steel corrosion rates (k_{corr}) after 120 minutes of immersion in 1M HCl with absence and presence of different concentrations of inhibitor A.

The following conclusions can be drawn from the impedance data give in tables (14,15):

1-The value of R_{ct} increases with increasing inhibitors concentrations, and hence, increasing the corrosion inhibition efficiency in acidic solution. This can be attributed to the formation of protective film on the metal/solution interface.⁽³³⁾

2-The existence of single semicircle was simply related to single charge transfer process occurred during dissolution of C-steel which unaffected by the presence of investigated compounds.

3-The value of double layer capacitance decreases by increasing the inhibitor concentration. This case was attributed to increase in thickness of electronic double layer and the replacement of adsorbed water molecules on C-steel surface by the inhibitor molecules. This will decrease the dielectric constant in the solution because C_{dl} is directly and inversely proportional to dielectric constant and thickness of electronic double layer respectively.

4-The coverage surface area (Θ) and inhibition efficiency (I.E. %) obtained from EIS measurements are nearly close to those obtained from weight loss technique. These confirm to us that inhibition efficiency; against C-Steel corrosion in 1M HCl, of inhibitor A major than B at the same conditions.

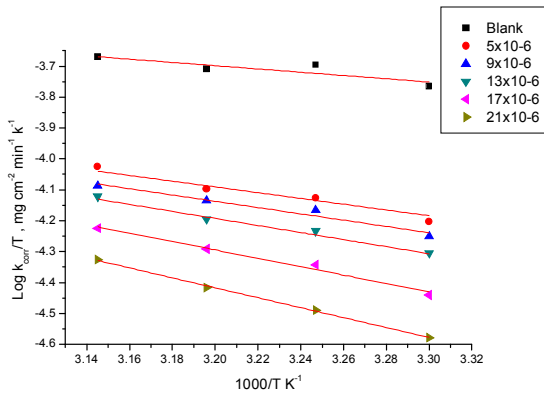


Figure (6): Transition-state for carbon steel corrosion rates (k_{corr}/T) in 1M HCl with absence and presence of different concentrations of Inhibitor A.

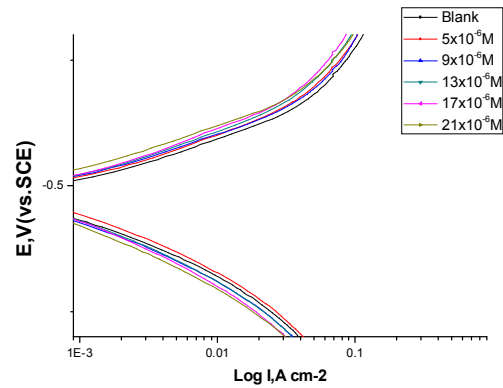


Figure (7): Potentiodynamic polarization curve for corrosion of carbon steel in 1M HCl at different concentration of inhibitor A at 30°C.

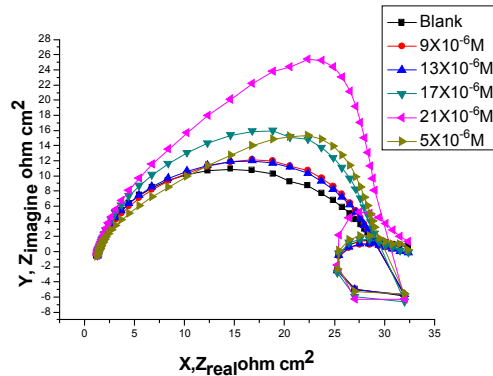


Figure (8): The Nyquist plots for the corrosion of carbon steel in 1M HCl with absence and presence of different concentrations of Inhibitor A at 30°C

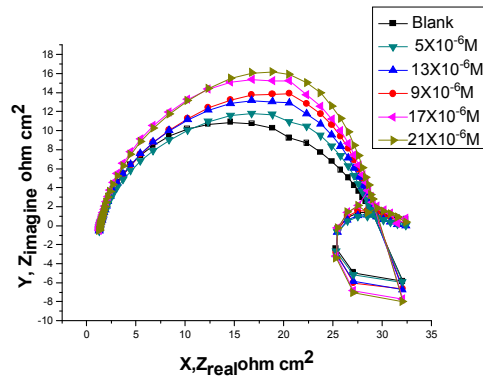


Figure (9): The Nyquist plots for the corrosion of carbon steel in 1M HCl with absence and presence of different concentrations of Inhibitor B at 30°C.

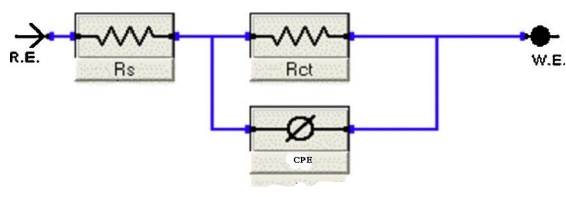


Figure (10): Equivalent circuit model used to fit experimental EIS 1M HCl

Conclusion:

1- The adsorption process of the investigated inhibitors A and B on C-steel surface in 1M HCl occurs through physisorption type.

2- The values of θ by inhibitors A and B could fit, Langmuir and Temkin adsorption isotherm respectively.

Table (14): EIS parameters for the corrosion of carbon steel in 1M HCl with absence and presence of different concentrations of inhibitor A at 30°C.

Concentration of inhibitor in M	C_{dl} μfcm^{-1}	R_{ct} Ωcm^2	θ	%I.E.
Blank	24.1	17.6	–	–
5×10^{-6}	9.664100002	43.89028431	0.599	59.9
9×10^{-6}	8.266300002	51.31195335	0.657	65.7
13×10^{-6}	6.868500001	61.75438596	0.715	71.5
17×10^{-6}	5.133300001	82.62910798	0.787	78.7
21×10^{-6}	3.8078000	111.3924051	0.842	84.2

Table (15): EIS parameters for the corrosion of carbon steel in 1M HCl in absence and presence of different concentrations of inhibitor B at 30° C.

Concentration of inhibitor in M HCl	C_{dl} μfcm^{-1}	R_{ct} Ωcm^2	θ	%I.E.
Blank	24.1	17.6	–	–
5×10^{-6}	10.8932	38.9380531	0.548	54.8
9×10^{-6}	10.0015	42.40963855	0.585	58.5
13×10^{-6}	8.2181	51.61290323	0.659	65.9
17×10^{-6}	7.4951	56.59163987	0.689	68.9
21×10^{-6}	6.1214	69.29133858	0.746	74.6

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