

INHIBITION OF C-STEEL BY SOME  
CYANOACETOHYDRAZIDE DERIV  
ATIVES IN HCL SOLUTION

A.S.Fouda<sup>a</sup>, M.Abdallah<sup>b</sup>, and A.Attia<sup>a</sup>

a) Department of Chemistry, Faculty of Science, El-Mansoura Univeristy,  
El-Mansoura-35516, EGYPT. - email: asfouda48@yahoo.com

b) Department of Chemistry, Faculty of Science, Benha Univeristy,  
Benha, EGYPT.

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ABSTRACT

This paper describes an investigation of the corrosion behavior of C-steel in 2M HCl solution in presence of some Cyanoacetohydrazide derivatives by weight loss, galvanostatic polarization, potentiodynamic anodic polarization techniques. The explore methods gave almost similar results. Results obtained reveal that inhibitor (I) is the best inhibitors and the inhibition efficiency (IE %) follows the sequence  $I > II > III > IV$ . The percentage inhibition efficiency was found to increase with increasing concentration of inhibitors and with decreasing the temperature of the medium. The addition of KI, KSCN, and KBr to Cyanoacetohydrazide derivatives enhanced the inhibition efficiency due to synergistic effect. The inhibitors are adsorbed on the C-steel surface according to Temkin's adsorption isotherm. Some thermodynamic functions were computed and discussed. It was found that the Cyanoacetohydrazide derivatives provide a good protection to C-steel against pitting corrosion in chloride ions containing solutions.

**Key words:** Cyanoacetohydrazide derivatives; corrosion; C-steel; HCl; pitting; quantum chemical calculation;

1. INTRODUCTION

C-steel, the most widely used engineering material, accounts for approximately 85% of the annual steel production world wide. Despite its

relatively limited corrosion resistance, C- steel is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal-processing equipment. The use of chemical inhibitors to decrease the rate of corrosion processes of carbon steels is quite varied [Babu et al., (2005); Fouda et al., (2005); Yurchenko et al.,(2006); Hossain et al., (2006) and Abd El-Wahaab et al., (2007)]. Generally nitrogen containing compounds work more effectively in HCl. Pyridine derivatives have been found as good inhibitors for corrosion of mild steel in acidic medium [Bouklah et al., (2005) and Abd El-Maksoud et al., (2005)]. Diazole based compounds [Ling-Guang et al., (2002) and Bouklah et al., (2005)] also work as a good corrosion inhibitors in HCl. Recent literature survey reveals that nitrogen containing compounds [Aguilar et al., (2006)] are potential inhibitors in acidic solution.

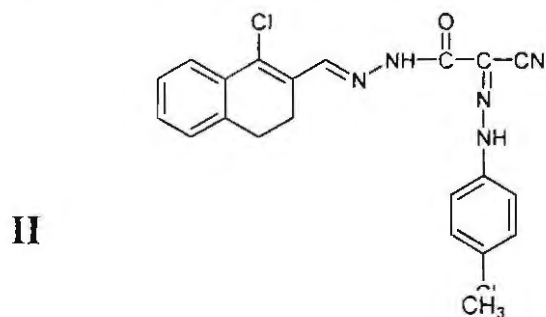
The present work was designed to study the corrosion inhibition of carbon steel in HCl solutions by new Cyanoacetohydrazide derivatives as corrosion inhibitors using three different techniques, and to use some anions to increase the % IE. The effect of temperature on the corrosion behavior also was investigated.

## 2. EXPERIMENTAL TECHNIQUES

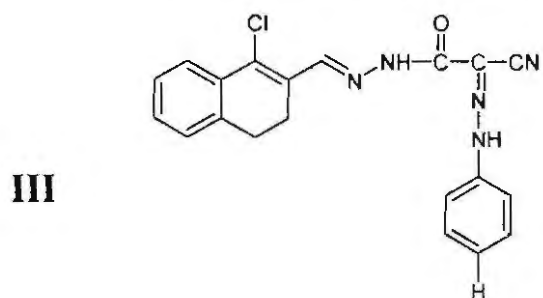
2 M HCl solutions were prepared from an analytical reagent grade of HCl 35.5 % and bi-distilled water and were used as corrosive media. All the experiments were performed at  $303 \pm 1$  K with C- steel samples with the composition (weight %): 0.200% C, 0.350% Mn, 0.024% P, 0.003% Si and the remainder iron. The inhibitors were synthesized in the laboratory following the procedure reported before [Lagrene et al., (2002)]. The structure of the investigated Cyanoacetohydrazide derivatives used is:



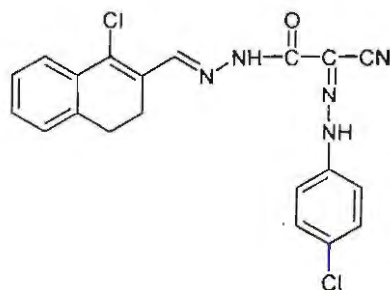
2-(2-(4-methoxyphenyl) hydrazono)- N-((4-chloro-1,2-dihydronapht-3-yl)methylene)-2-cyanoacetohydrazide



2-(2-(4-methylphenyl) hydrazono)-N-((4-chloro-1,2-dihydronapht-3-yl)methylene)-2-cyanoacetohydrazide



2-(2-(phenyl hydrazono)-N-((4-chloro-1,2-dihydronapht-3-yl)methylene)-2-cyanoacetohydrazide



## IV

2-(2-(4-chlorophenyl hydrazono)-N-((4-chloro-1,2-dihydronaphth-3-yl)methylene)-2-cyanoacetohydrazide

### 2.1. Weight loss method

C-steel specimens of dimensions 2 x 2 x 0.2 cm, in triplicate were mechanically polished successively with different grades emery papers, up to 1200 grade, degreased in acetone rinsed with bi-distilled water and finally dried then immersed in 100 ml of 2M HCl solutions containing various concentrations of the inhibitors. The weight of the specimens before and after immersion was determined. The weight loss was used to calculate the percentage inhibition efficiency (% IE) using the equation:

$$\% IE = \frac{W - W'}{W} \times 100 \quad (1)$$

where:  $W$  and  $W'$  are the weight losses ( $\text{mg cm}^{-2}$ ) of C-steel in 2M HCl in the absence and presence of different concentrations of inhibitor, respectively.

### 2.2- Electrochemical technique (Galvanostatic polarization method)

Cell with three different types of electrodes [Elayyachy et al., (2002)] was used during polarization measurements: The working electrode was C-steel electrode, which cut from C-steel sheets. The electrodes were of dimensions 1cm x 1cm and were weld from one side to a copper wire used for electrical connection. The samples were embedded in glass tube using epoxy resin. Saturated calomel electrode (SCE) and a platinum coil as reference and auxiliary electrodes, respectively, were used.

A constant quantity of the test solution (100 ml) was taken in the polarization cell. A time interval of about 30 minutes was given for the



system to attain a steady state. Both cathodic and anodic polarization curves were recorded galvanostatically using Amel Galvanostat (Model-549) and digital Multimeters (Fluke-73) were used for accurate measurements of potential and current density. All the experiments were carried out at  $30 \pm 1^\circ\text{C}$  using ultra circulating thermostat.

% IE was calculated using the equation:

$$\% IE = \frac{i_{corr} \tilde{i}'_{corr}}{i_{corr}} \times 100 \quad (2)$$

where:  $i_{corr}$  and  $i'_{corr}$  are the corrosion current densities in the absence and presence of the inhibitors, respectively.

### 2.3-Potentiodynamic anodic polarization

Potentiodynamic anodic polarization technique was performed at a scanning rate of 1 mV/s using a Wenking potentiostat type POS 73 and the current density-potential curves were recorded on X-Y recorder type PL.3. The potential were measured relative to a saturated calomel electrode (SCE) and the electrolytic cell used is the same as in 2.2.

## 3. RESULTS

### 3.1. Weight loss

Weight loss of C-steel, in  $\text{mg cm}^{-2}$  of the surface area, was determined at various time intervals in the absence and presence of different concentrations ( $1 \times 10^{-6}$ - $11 \times 10^{-6}$  M) of cyanoacetohydrazide derivatives (I-IV). The curves obtained in the presence of different concentrations of inhibitors fall significantly below that of free acid. Similar behaviors were obtained for the other inhibitors. Values of % IE are tabulated in Table 1. In all cases, the increase in the inhibitor concentration was accompanied by a decrease in the weight loss and an increase in % IE. These results lead to the conclusion that, these compounds under investigation are fairly efficient as inhibitors for C-steel dissolution in HCl solution. Careful inspection of these results showed that, at the same inhibitor concentration, the ranking of the inhibitors according to % IE is as follow:

$$\text{I} > \text{II} > \text{III} > \text{IV}$$

**Synergistic effect**

The effect of addition  $1 \times 10^{-2}$  M KSCN, KI and KBr on the corrosion rate of C- steel in the absence and presence of different concentrations of inhibitors (I-IV) in 2M HCl solutions was investigated using weight loss method. Results of % IE obtained are summarized in Table 2. It was observed from these results that these additives improved the % IE significantly. The interactions of these additives with the inhibitor molecules can be described by introduction of the synergistic parameter ( $S_{\theta}$ ) which is defined as [Abd El-Haleem et al., (1985)]:

$$S_{\theta} = \frac{1 - \theta_{1+2}}{1 - \theta'_1 - \theta'_2} \quad (3)$$

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

$\theta_1$  = the degree of surface coverage by the anions

$\theta_2$  = the degree of surface coverage by the cations

$\theta'_{1+2}$  = measured surface coverage by both anions and cations.

$S_{\theta}$  approaches 1 when no interaction between the inhibitor compounds exists, while  $S_{\theta} > 1$  points to a synergistic effect. In the case of  $S_{\theta} < 1$ , the antagonistic interaction prevails.

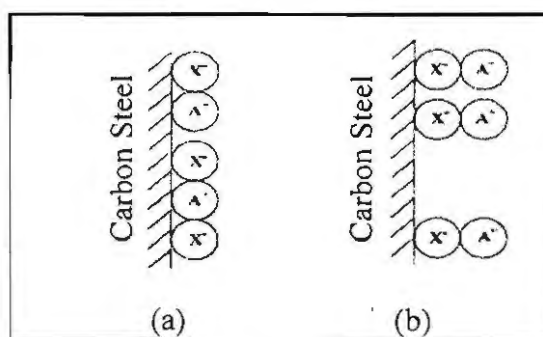
**Table (1):** % Inhibition efficiency of C-steel dissolution at 90 min immersion in 2 M HCl in the presence of different concentrations of inhibitors at 30°C.

Conc., M	% IE			
	(I)	(II)	(III)	(IV)
$1 \times 10^{-6}$	67.4	62.3	57.7	43.1
$3 \times 10^{-6}$	70.5	64.7	58.2	45.9
$5 \times 10^{-6}$	73.1	68.1	64.5	50.7
$7 \times 10^{-6}$	76.0	73.1	64.7	54.0
$9 \times 10^{-6}$	77.3	73.1	68.5	54.3
$11 \times 10^{-6}$	80.5	75.2	71.1	58.7

**Table (2):** %Inhibition efficiency of C-steel dissolution at 90 min. immersion in 2 M HCl in the presence of  $1 \times 10^{-2}$  M KI at different concentrations of inhibitors at  $30^\circ\text{C}$ .

Conc., M	% IE			
	(I)	(II)	(III)	(IV)
$1 \times 10^{-6}$	79.3	70.5	65.9	59.2
$3 \times 10^{-6}$	82.2	72.3	68.7	61.1
$5 \times 10^{-6}$	83.9	77.2	71.3	65.3
$7 \times 10^{-6}$	86.9	78.9	74.3	69.5
$9 \times 10^{-6}$	89.4	84.3	78.5	72.4
$11 \times 10^{-6}$	90.2	85.3	80.0	75.3

Values of  $S_\theta$  summarized in Tables 3 are more than unity, suggesting that the phenomenon of synergism exists between the inhibitors and these additives used. Aramaki [Larabi et al., (2004) and Aramaki et al., (1987)] has proposed two kinds of joint adsorption (competitive and cooperative) to explain the synergistic action observed between an anion and a cation. For competitive adsorption, the anion and cation are adsorbed at different sites on the electrode surface and for cooperative adsorption, the anion is chemisorbed on the surface and the cation is adsorbed on the layer of the anions. The two types of adsorption are represented schematically in Fig. 1 and can be characterized by a synergistic factor ( $S_\theta$ ) calculated as above.



**Fig. (1):** Schematic representations of (a) competitive and (b) cooperative adsorption of the anions ( $X^-$ ) and cations ( $A^+$ ) on carbon steel surface in acid solutions.



The synergistic inhibitive effect brought about by combination of the inhibitors with KSCN, KI and KBr for the corrosion of C- steel in 2 M HCl can be explained as follows: The strong chemisorption of  $X^-$  ions ( $SCN^-$ ,  $I^-$  or  $Br^-$ ) on the metal surface is responsible for the synergistic effect of these ions, in attraction with protonated inhibitor [Ochoa et al., (2004)].  $X^-$  ions are adsorbed on the anodic sites on the metal surface. Surface charge is changed to negative by the specific adsorption of these ions resulting in the joint adsorption of anions with the inhibitor cations. The inhibitors are believed to be adsorbable, not only on the cathodic sites by coulombic attraction using the charge of the protonated molecule, but also on the anodic sites by virtue of donation of the electron-pair on the nitrogen or chloride atoms of the unprotonated molecule [Bentiss et al., (2002)] therefore, interference adsorption can take place at the anodic sites.

**Table (3):** Synergism parameter ( $S_0$ ) for different concentrations of inhibitors for C-steel dissolution in 2M HCl with addition of  $1 \times 10^{-2}$  M KI at 30°C.

Conc., M	Synergism parameter ( $S_0$ )			
	(I)	(II)	(III)	(IV)
$1 \times 10^{-6}$	1.1	1.0	1.1	1.1
$3 \times 10^{-6}$	1.3	1.2	1.1	1.5
$5 \times 10^{-6}$	1.4	1.3	1.0	1.2
$7 \times 10^{-6}$	1.5	1.0	1.1	1.3
$9 \times 10^{-6}$	1.7	1.3	1.3	1.4
$11 \times 10^{-6}$	1.5	1.3	1.4	1.3

#### Adsorption isotherm

Assuming the corrosion inhibition was caused by the adsorption of cyano acetohydrazide derivatives, and the values of surface coverage for different concentrations of inhibitors in 2M HCl were evaluated from Weight loss measurement using the following equation:

$$\Theta = [\text{Weight loss}_{(\text{pure})} - \text{Weight loss}_{(\text{inh.})} / \text{Weight loss}_{(\text{pure})}] \quad (4)$$

From the values of ( $\theta$ ), it can be seen that the values of ( $\theta$ ) increased with increasing the concentration of cyanoacetohydrazide



derivatives. Using these values of surface coverage, one can utilize different adsorption isotherms to deal with experimental data.

The Temkin's adsorption isotherm was applied to investigate the adsorption mechanism, by plotting ( $\theta$ ) vs.  $\log c$ , a straight line was obtained. On the other hand, it is found that Kinetic-thermodynamic model of El Awady et al [El-Awady et al., (1985)] which has the formula:

$$\text{Log } (\theta/1 - \theta) = \text{log } K' - y \text{ log } C \quad (5)$$

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 cyanoacetohydrazide molecule and  $C$  is the bulk concentration of the inhibitor.

From Table (4) it is noted that  $\Delta G_{\text{ads}}$  values have a negative sign indicating that the adsorption process proceeds spontaneously, and increase as the percentage inhibition increases.

**Table (4):** Inhibitor equilibrium constant ( $K$ ), free energy of adsorption ( $\Delta G_{\text{ads}}$ ), number of active sites ( $1/y$ ) and later interaction parameter ( $a$ ) for inhibitors at 30°C.

Inhibitors	Kinetic model			Temkin		
	$1/y$	$K$	$-\Delta G_{\text{ads}}$ , $\text{kJmol}^{-1}$	$a$	$K$	$-\Delta G_{\text{ads}}$ , $\text{kJmol}^{-1}$
(I)	3.203	0.975	62.7	14.03	70.3	64.7
(II)	3.124	0.984	59.8	12.30	61.3	63.7
(III)	3.053	0.755	55.3	13.29	27.1	54.3
(IV)	3.887	0.474	51.9	13.73	2.54	39.8

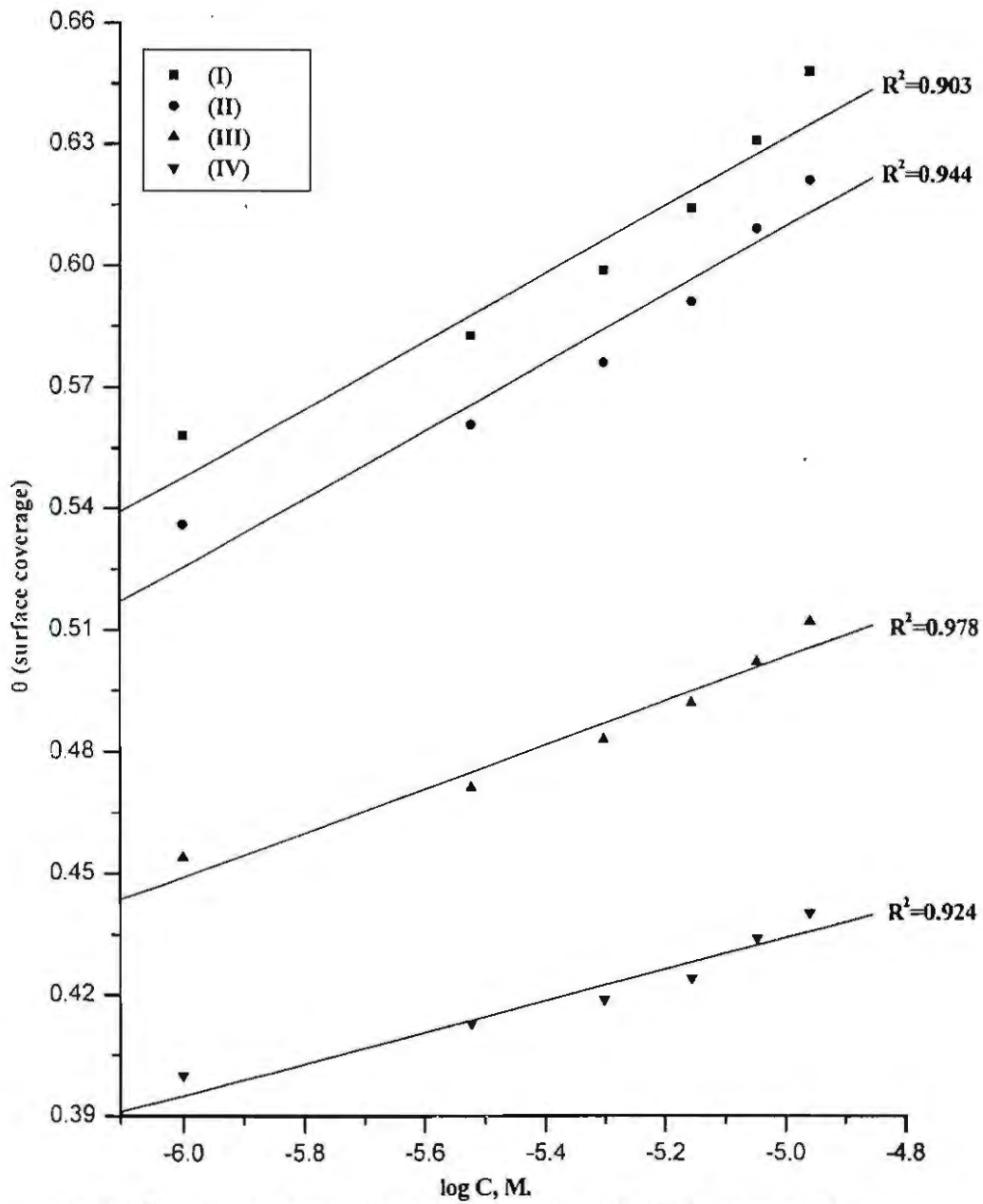


Fig. (2): Curve fitting of corrosion data for C-steel in 2M HCl in presence of different concentrations of inhibitors to the Temkin isotherm at 30°C.

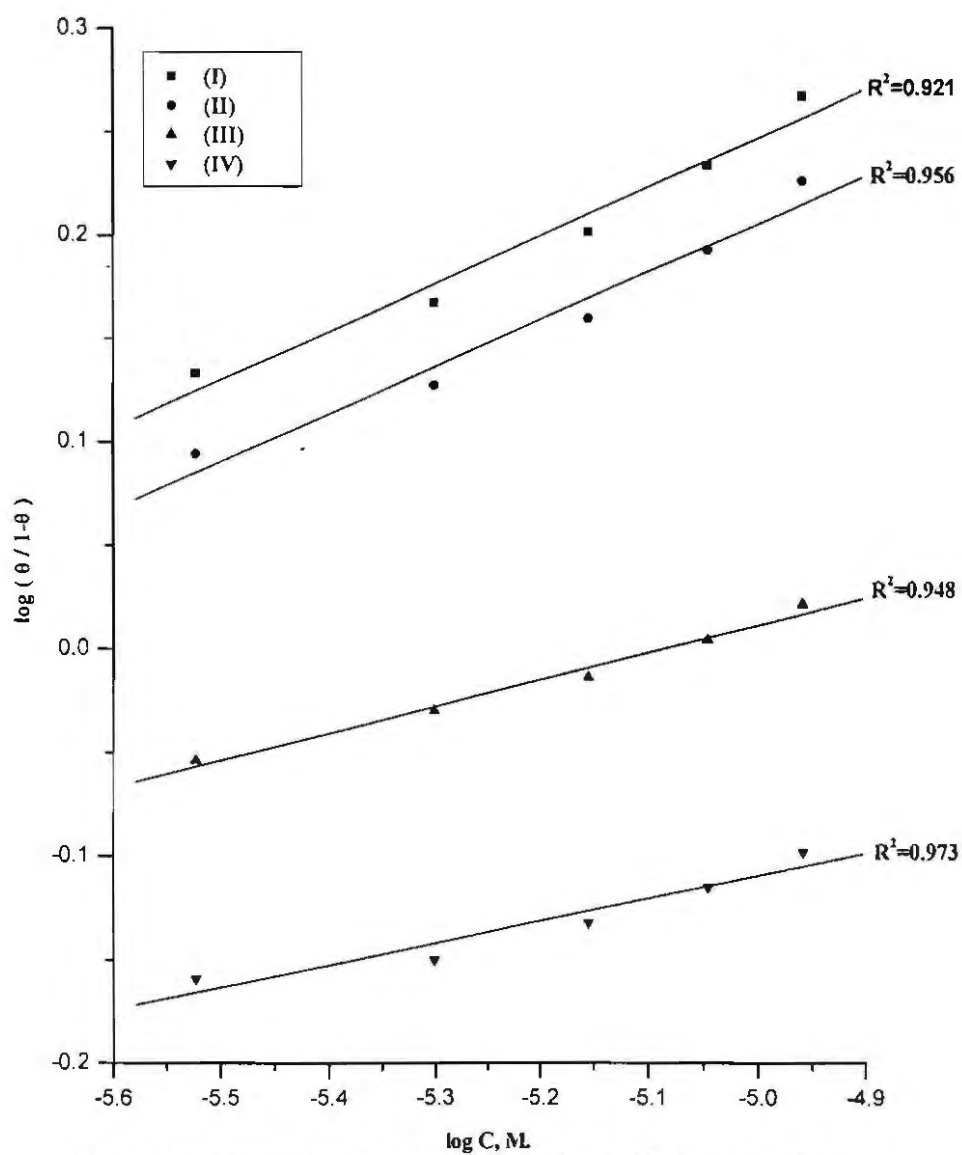


Fig. (3): Curve fitting of corrosion data for C-steel in 2M HCl in presence of different concentrations of inhibitors to the kinetic model at 30°C.



**Effect of temperature**

Corrosion reactions are usually regarded as Arrhenius processes and the rate ( $k$ ) can be expressed by the relation:

$$\log k = A - \frac{E_a}{2.303 RT} \quad (6)$$

where:  $E_a$  is the activation energy of the corrosion process  $R$  is the universal gas constant,  $T$  is the absolute temperature and  $A$  is the Arrhenius pre-exponential constant depends on the metal type and electrolyte. Arrhenius plots of  $\log k$  vs.  $1/T$  for carbon steel in 2M HCl in the absence and presence of  $11 \times 10^{-6}$  M of inhibitors (I-IV) are shown graphically in Fig. 3. The variation of  $\log k$  vs.  $1/T$  is a linear one and the values of  $E_a$  obtained are summarized in Table 5. These results show that the almost similar values of  $E_a$  ranging from 52 to 73  $\text{kJ mol}^{-1}$  suggest that the inhibitors are similar in the mechanism of action. The increase in  $E_a$  with the addition of  $11 \times 10^{-6}$  M of inhibitors (I-IV) indicating that the energy barrier for the corrosion reaction increases. It is also indicated that the whole process is controlled by surface reaction, since the activation energy of the corrosion process is over 20  $\text{kJ mol}^{-1}$  [Bensajjay et al., (1985)] Enthalpy and entropy of activation ( $\Delta H^*$ ,  $\Delta S^*$ ) are calculated from transition state theory using the equation [7]:

$$k = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (7)$$

where:  $h$  is Planck's constant,  $N$  is Avogadro's number. A plot of  $\log k/T$  vs  $1/T$  also gave straight lines as shown in Fig. 4 for carbon steel dissolution in 2M HCl in the absence and presence of  $11 \times 10^{-6}$  M of inhibitors (I-IV). The slopes of these lines equal  $-\Delta H^*/2.303R$  and the intercept equal  $\log RT/Nh + (\Delta S^*/2.303R)$  from which the value of  $\Delta H^*$  and  $\Delta S^*$  were calculated and tabulated in Table 5. From these results, it is clear that the presence of the tested compounds increased the activation energy values and consequently decreased the corrosion rate of the carbon steel. These results indicate that these tested compounds acted as inhibitors through increasing activation energy of carbon steel dissolution by making a barrier to mass and charge transfer by their adsorption on carbon steel surface. The values of  $\Delta H^*$  reflects the strong adsorption of these compounds on carbon steel surface. The values of  $\Delta S^*$  in the

absence and presence of the tested compounds are large and negative; this indicates that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex and the activated molecules were in higher order state than that at the initial state [Haladky et al., (1980)].

**Table (5):** Effect of concentrations of inhibitors on the activation thermodynamic parameters of C-steel dissolution in 2M HCl.

Inhibitor	Concentration, M	$E_a^*$ , kJ mol <sup>-1</sup>	$\Delta H^*$ , kJ mol <sup>-1</sup>	$-\Delta S^*$ , J mol <sup>-1</sup> K <sup>-1</sup>
Blank	0.0	52.0	51.4	81.4
I	$1 \times 10^{-6}$	85.0	86.4	7.3
	$3 \times 10^{-6}$	93.4	89.5	13.3
	$5 \times 10^{-6}$	95.1	92.2	20.9
	$7 \times 10^{-6}$	95.6	91.6	21.5
	$9 \times 10^{-6}$	96.3	93.3	25.9
	$11 \times 10^{-6}$	97.0	94.3	25.6
II	$1 \times 10^{-6}$	79.6	76.8	25.0
	$3 \times 10^{-6}$	80.0	78.7	19.7
	$5 \times 10^{-6}$	83.2	80.5	14.3
	$7 \times 10^{-6}$	84.0	81.3	12.5
	$9 \times 10^{-6}$	84.0	82.6	8.8
	$11 \times 10^{-6}$	85.1	83.4	7.4
III	$1 \times 10^{-6}$	67.8	71.4	41.0
	$3 \times 10^{-6}$	74.1	71.9	36.7
	$5 \times 10^{-6}$	75.2	74.0	33.4
	$7 \times 10^{-6}$	76.8	75.4	28.5
	$9 \times 10^{-6}$	78.2	79.3	17.3
	$11 \times 10^{-6}$	80.2	80.2	13.3
IV	$1 \times 10^{-6}$	61.4	67.0	54.2
	$3 \times 10^{-6}$	70.2	67.1	53.3
	$5 \times 10^{-6}$	70.9	68.2	51.6
	$7 \times 10^{-6}$	71.9	69.1	47.8
	$9 \times 10^{-6}$	72.8	69.8	47.3
	$11 \times 10^{-6}$	73.0	70.1	46.1

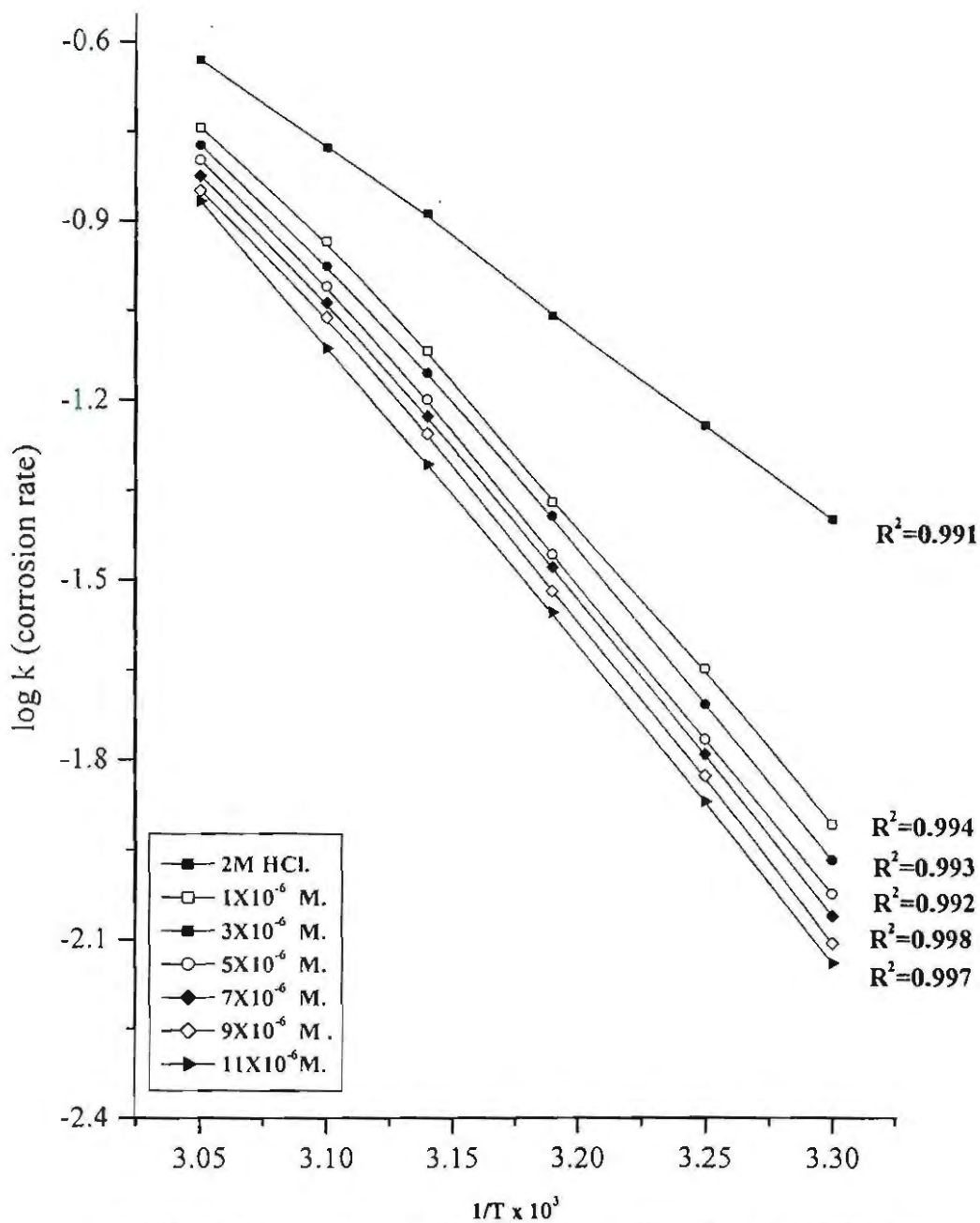


Fig. (4):  $\log k$  (corrosion rate) -  $1/T$  curves for c-steel dissolution in 2M HCl in absence and presence of different concentrations of inhibitor (I).



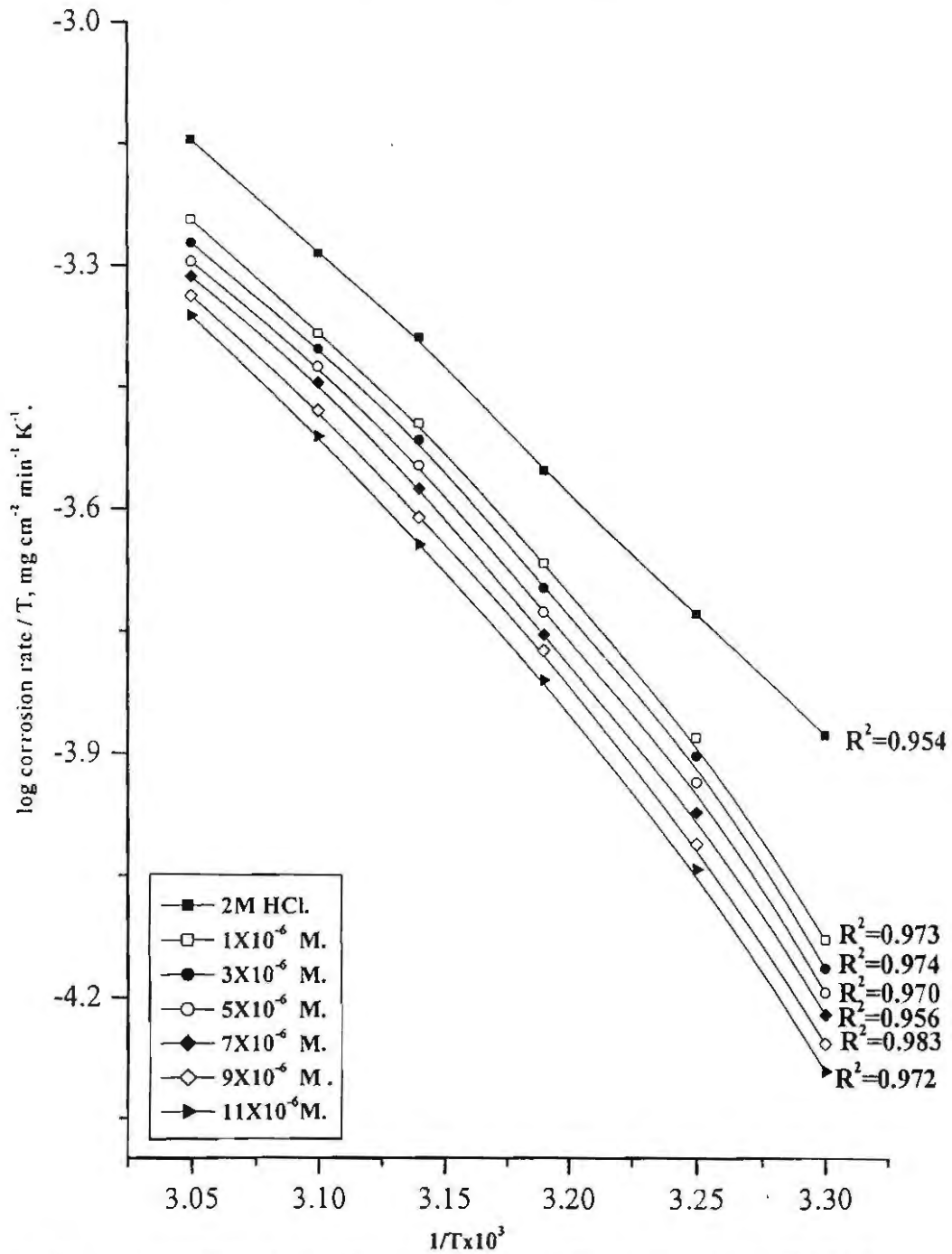


Fig. (5): log (corrosion rate/T) - (1/T) curves for C-steel dissolution in 2M HCl in absence and presence of different concentrations of inhibitor (IV).

**Galvanostatic measurement**

Fig (6) shows the galvanostatic polarization curves (E vs. log i) of C-steel dissolution in 2M HCl, in the presence of different concentrations of compound (I). An increase in the concentration, of inhibitor shifted the polarization curves towards more negative potentials for cathodic Tafel lines, and towards more positive potentials for anodic Tafel lines. Polarization data suggested that the additives used act as mixed-type inhibitors, because the values of negative shift are equal to the values in the positive shift in  $E_{corr}$ . The corrosion kinetic parameters such as corrosion current density ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ), cathodic Tafel slopes ( $\beta_c$ ), anodic Tafel slopes ( $\beta_a$ ), degree of surface coverage ( $\theta$ ) and percentage inhibition(% IE) were derived are recorded in Table (6).

**Table (6):** Corrosion parameters of C-steel in 2M HCl at 30°C in absence and the presence of various concentrations of inhibitors (I–IV).

Inhibitors types	Conc., M.	$-E_{corr}$ mV	$I_{corr}$ $\mu A$ $cm^{-2}$	$\beta_a$ mVdec <sup>-1</sup>	$\beta_c$ mVdec <sup>-1</sup>	$\theta$	% IE
Blank	2MHCl	532	1.970	200	162	-	-
I	$1 \times 10^{-6}$	507	0.878	200	190	0.5543	55.43
	$3 \times 10^{-6}$	509	0.837	201	202	0.5750	57.50
	$5 \times 10^{-6}$	513	0.801	206	205	0.5930	59.30
	$7 \times 10^{-6}$	511	0.721	206	203	0.6340	63.40
	$9 \times 10^{-6}$	516	0.697	205	198	0.6460	64.40
	$11 \times 10^{-6}$	520	0.579	201	197	0.7060	70.60
II	$1 \times 10^{-6}$	506	0.882	203	197	0.5522	55.22
	$3 \times 10^{-6}$	511	0.833	204	201	0.5771	57.71
	$5 \times 10^{-6}$	513	0.773	210	216	0.6076	60.76
	$7 \times 10^{-6}$	515	0.711	211	208	0.6390	63.90
	$9 \times 10^{-6}$	517	0.667	217	198	0.6614	66.14
	$11 \times 10^{-6}$	519	0.610	208	206	0.6903	69.03
III	$1 \times 10^{-6}$	515	1.07	210	209	0.4568	45.68
	$3 \times 10^{-6}$	517	1.031	206	208	0.4766	47.66
	$5 \times 10^{-6}$	517	0.981	203	208	0.5020	50.20
	$7 \times 10^{-6}$	516	0.942	203	211	0.5218	52.18
	$9 \times 10^{-6}$	511	0.871	209	214	0.5578	55.78
	$11 \times 10^{-6}$	512	0.782	223	207	0.6030	60.30
IV	$1 \times 10^{-6}$	507	1.09	197	198	0.4467	44.67
	$3 \times 10^{-6}$	501	1.038	198	205	0.4730	47.30
	$5 \times 10^{-6}$	513	0.987	203	216	0.4989	49.89
	$7 \times 10^{-6}$	510	0.951	203	207	0.5172	51.72
	$9 \times 10^{-6}$	502	0.891	207	199	0.5477	54.75
	$11 \times 10^{-6}$	491	0.793	191	202	0.5974	59.74

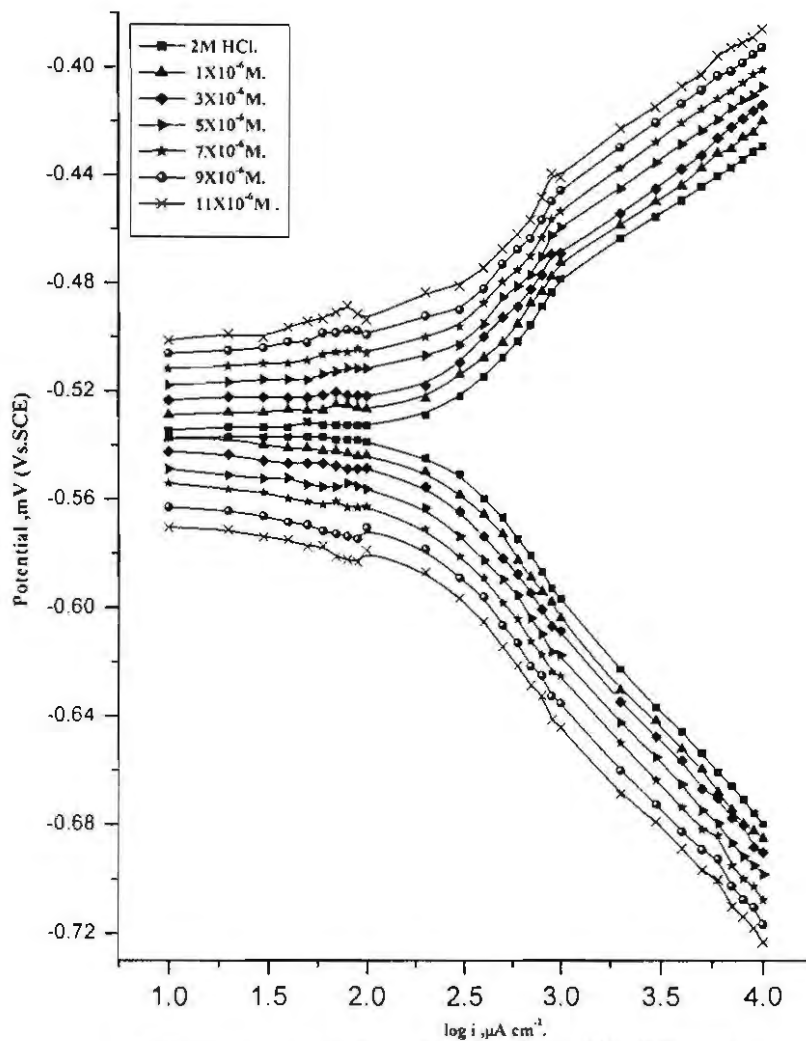


Fig.(6):Galvanostatic polarization curves of C-steel in 2M HCl in absence and presence of inhibitor (I) at various concentrations at 30°C.



### Pitting corrosion

The effect of addition of increasing concentrations of some cyano acetohydrazide derivatives on the potentiodynamic anodic polarization curves of C-steel electrode in 0.1M NaCl (as a pitting corrosion agent) at a scanning rate of 1mV/sec was studied. It was found that the pitting potential of the C-steel electrode is shifted to more positive (noble) values with increasing the concentration of additives. This indicates an increasing resistance to pitting attack.

Fig. (7) Represents the relationship between pitting potential ( $E_{pitt.}$ ) and the logarithmic of the molar concentration ( $\log C$ ) of the added compounds. Straight lines were obtained and the following conclusions can be drawn:

- a) An increase in inhibitor concentration causes the shift of the pitting potential into more positive values in accordance with the following equation :

$$E_{pitt.} = a_2 + b_2 \log C_{inh.} \quad (8)$$

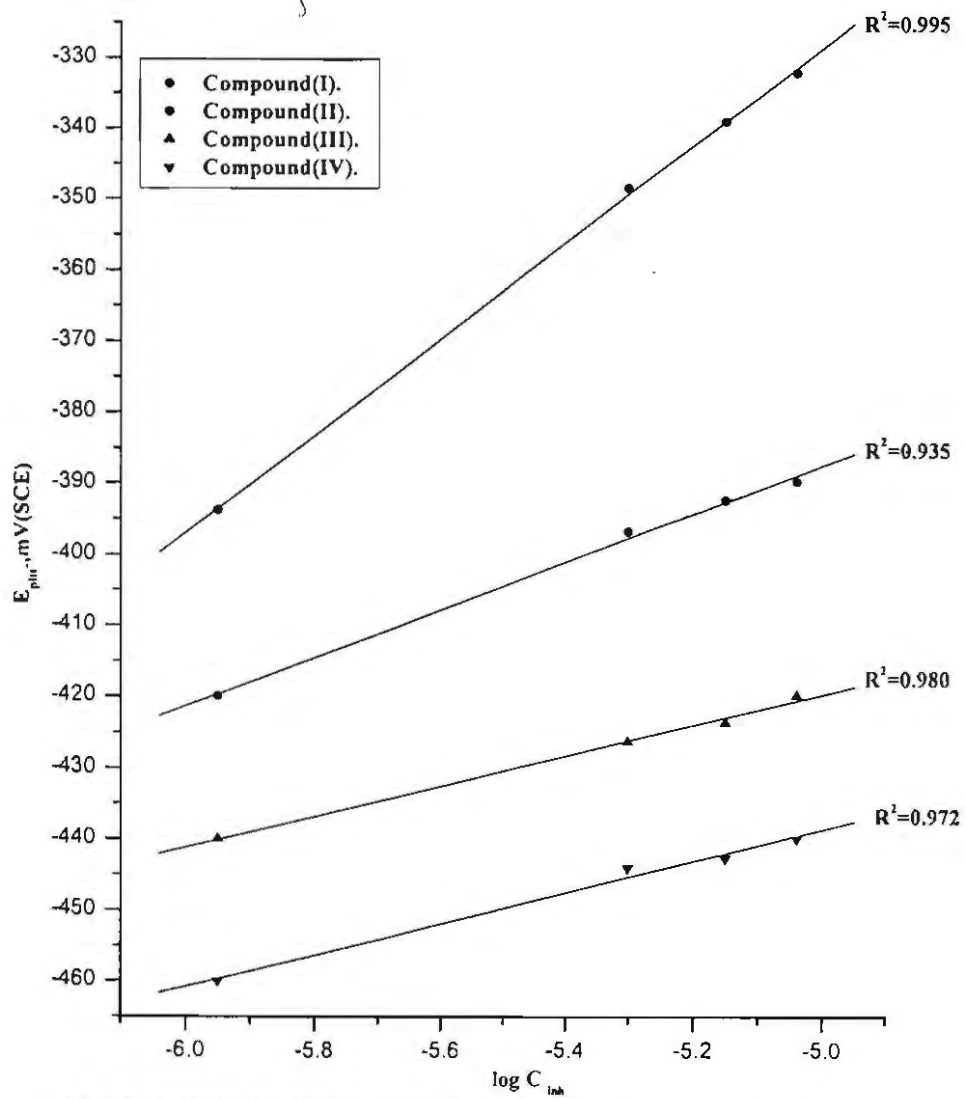
where  $a_2$  and  $b_2$  are constants which depend on both the composition of additives and the nature of the electrode.

- b) Inhibition afforded by these compounds using the same different concentrations of the additives decreases in the order :

$$I > II > III > IV$$

The adsorbed molecule may inhibit the pitting corrosion by shifting the critical pitting potential to more noble value by one or a combination of the following mechanisms:

- i) Forming a physical barrier layer between metal and coordinate.
- ii) Reducing the metal reacting through an alteration in the nature of metal surface.
- iii) Changing the structure of the metal / solution interface.



Fig(7): The relationship between pitting potential of C-Steel and logarithm the concentration of the additives in presence of 0.1 M NaCl

**Quantum-chemical study**

The results obtained from the relation between inhibition characteristics and quantum chemical data show that  $\log i_{\text{corr}}$  mostly depends upon the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Fig. (8) shows that the inhibition efficiency increases with the increase of energy of the HOMO, that is, the increase of the ionization potential. It is further evident that the inhibition efficiency increases with the decrease of ionization of the molecule, which means that the molecule acts as an electron donor when blocking the corrosion reaction. The results of Table (7) show that the energies of HOMO orbital of the cyanoacetohydrazide derivatives decrease in the following order:

$$(I) > (II) > (III) > (IV)$$

Table (7): Quantum chemical parameters of  $9 \times 10^{-6}$  M of the cyanoacetohydrazide derivatives

Inhibitor	$\log i_{\text{corr}}$	HOMO energy Kcalmol <sup>-1</sup>	LUMO energy Kcalmol <sup>-1</sup>	%IE
I	1.0599	-7.2126	-1.13847	64.40
II	1.1361	-7.6654	-1.24177	66.14
III	1.1571	-7.7270	-1.26047	55.78
IV	1.2721	-7.8830	-1.2712	54.75

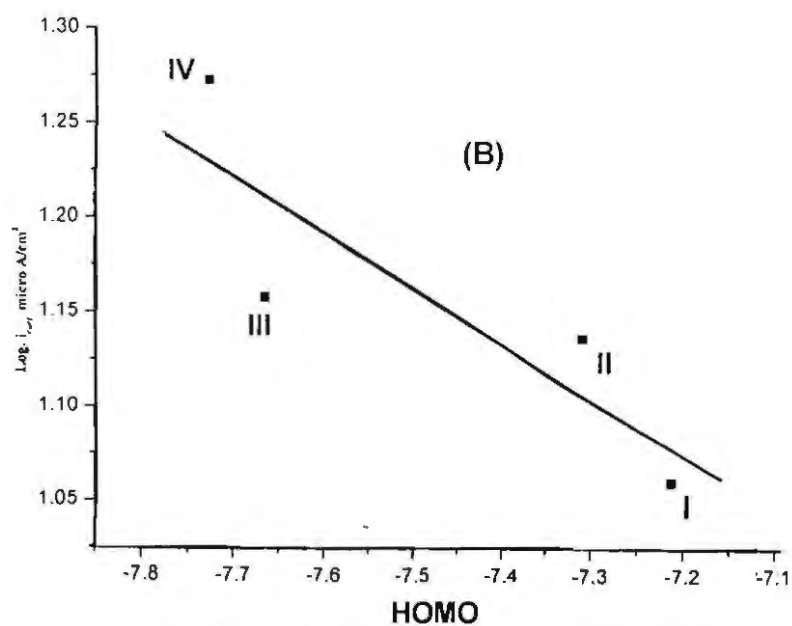
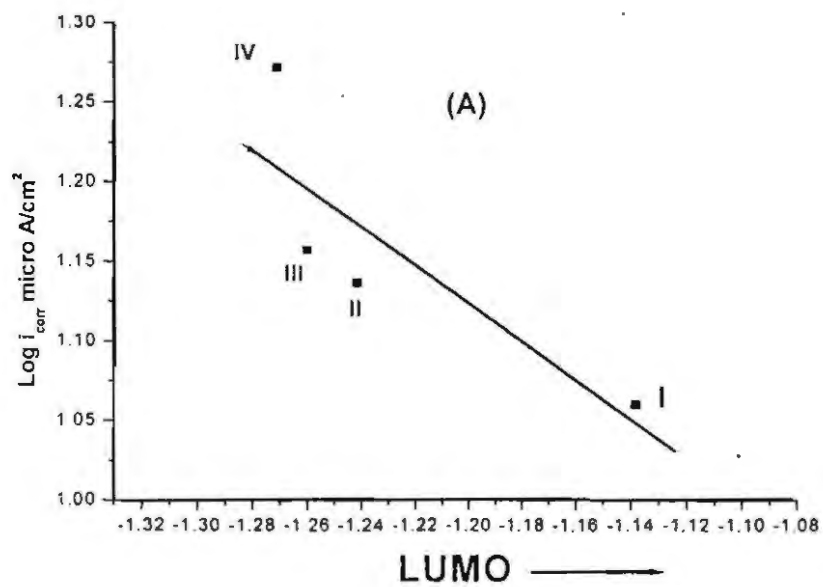


Fig. (8) Correlation of LUMO (A) and HOMO (B) energies with energies with  $\log i_{\text{corr}}$  for the investigated compounds



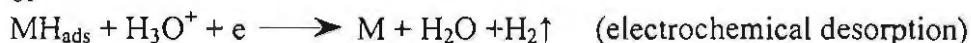
#### 4. Corrosion inhibition mechanism

From the previous results of various experimental techniques used, it was concluded that cyanoacetohydrazide derivatives (I-IV) inhibit the corrosion of carbon steel in 2M HCl, by adsorption at the metal/solution interface. A skeletal representation of the proposed mode of adsorption of studied compounds is shown in Fig. 8 and clearly indicates the active adsorption centers. The adsorption of these inhibitors can be explained in the following manner:

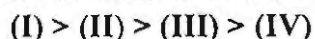
$M + H_3O^+ + e \longrightarrow H_2O + MH_{ads}$  (discharge step) where: M is the cathode metal surface, followed by either:



or



It was concluded that the mode of adsorption depends on the affinity of the metal towards the  $\pi$ -electron clouds of the ring system. Metals such as Cu and Fe, which have a greater affinity towards aromatic moieties, were found to adsorb benzene rings in a flat orientation. The order of decreasing the inhibition efficiency of the investigated compounds in the corrosive solution is as follows:



Compound (I) exhibits excellent inhibition power due to: (i) the presence of p-OCH<sub>3</sub> group which is an electron donating group with negative Hammett constant ( $\sigma = -0.27$ ), Also this group will increase the electron charge density on the molecule, (ii) its larger molecular size that may facilitate better surface coverage, and (ii) its adsorption through four active centers as shown from Fig (9).

Compound (II) comes after compound (I) in inhibition efficiency due to: (i) its lower molecular size than compound (I), (ii) its adsorption through three active centers, and (iii) the presence of p-CH<sub>3</sub> with low Hammett constant than p-OCH<sub>3</sub> ( $\sigma = -0.17$ ) which is highly electron releasing group which enhance the delocalized  $\pi$ -electrons on the active centers of the compound.

Compound (III) comes after compound (II) in inhibition efficiency inspite of it has three active centers, because it has lower molecular size than compound (II) and has no substituent in p-position (H-atom with  $\sigma = 0.0$ ) which contributes no charge density to the molecule.

Compound (IV) has the lowest inhibition efficiency. This is due to it has three active centers and the lowest molecular size. Also, the

presence of p- Cl which has positive Hammett constant ( $\sigma=+0.23$ ), i.e. group which lower the electron density on the molecule and hence, lower inhibition efficiency.

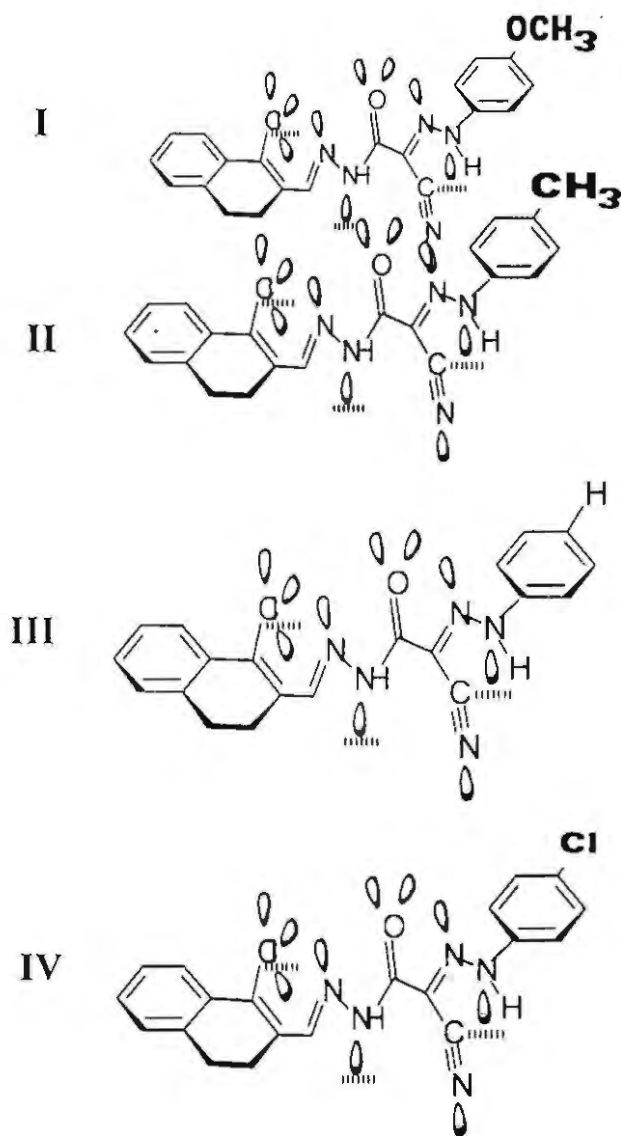


Fig. (9):skeleton representation of the adsorption mode aceto-hydrazone derivatives.

## 5. CONCLUSIONS

- (1) The investigated cyanoacetohydrazide derivatives act as inhibitors for carbon steel in 2M HCl.
- (2) The %IE increased with the increase in inhibitor concentration. At all used concentrations, %IE followed the order: **I > II > III > IV**.
- (3) The compounds are of mixed type inhibitors but the cathode is more polarized than the anode, i.e. they affect both anodic dissolution of carbon steel and hydrogen evolution reactions.
- (4) The adsorption of the investigated compounds was found to follow the Temkin's adsorption isotherm indicating that the inhibition process occurs via adsorption.
- (5) The thermodynamic parameters point toward both physisorption (major contributor) and chemisorption (minor contributor) of the inhibitors onto the metal surface. The negative values of  $\Delta G_{\text{ads}}^{\circ}$  obtained from this study indicate that these compounds are strongly spontaneously adsorbed on the carbon steel surface.
- (6) The presence of some anions in combination with inhibitors increases the %IE.
- (7) The %IE obtained from weight loss, polarization curves, pitting and quantum chemical calculations are in good agreement.

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المخلص العربي

تم دراسة التأثير المثبط لمشتقات السيانو اسيتوهيدريزيد على تاكل الصلب الكربوني في ٢ مولر حمض الهيدروكلوريك عند ٣٠م بطريقتي الفقد في الوزن والاستقطاب الجلفانوستاتيكي. وقد دلت طريقة الاسيقتاب الجلفانوستاتيكي على ان هذه المشتقات تعمل كمثبطات مختلطة وان ادمصاص هذه المركبات على سطح الصلب الكربوني تتبع ايزوثرم تمكن. وتقل كفاءة التثبيط بارتفاع درجة الحرارة مما يدل ان ادمصاص هذه المركبات على سطح الصلب الكربوني ادمصاص فيزيائي. وقد تم اضافة ايونات اليوديد والبروميد والنيوثينات على التركيزات المختلفة من هذه المشتقات ووجد أنها تزيد من كفاءة تثبيط هذه المشتقات.

