

HYDRAZONE DERIVATIVES AS CORROSION INHIBITORS FOR CARBON STEEL IN 1 M HCl SOLUTIONS

A. S. Fouda and D. M. Sobh

Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura, 35516, Egypt, Te: +2 050 2365730; Fax: +2 050 224678, 1E-mail addresses: asfouda@hotmail.com OR asfouda@mans.edu.eg (A. S. Fouda)

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ABSTRACT

Corrosion inhibition by some hydrazone derivatives on carbon steel in 1 M HCl solution has been investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and weight loss techniques. It was found that the inhibition efficiencies of hydrazone derivatives increased with increase in concentration of inhibitors but decreased with rise in temperature. Changes in impedance parameters (R_{ct} and C_{dl}) were indicative of the adsorption of hydrazone derivatives on the carbon steel surface. Adsorption of these compounds on carbon steel surface in 1 M HCl followed a Temkin adsorption isotherm. A physical adsorption phenomenon is proposed. Potentiodynamic polarization studies clearly revealed that these compounds act as mixed-type inhibitors retarding the anodic and cathodic corrosion reactions and do not change the mechanism of either hydrogen evolution reaction or carbon steel dissolution. Some kinetic parameters are obtained. (E_a) and other thermodynamic parameters for corrosion process have been calculated and discussed. Some quantum chemical parameters and the Mulliken charge densities on the optimized structure of hydrazone derivatives were also calculated. The results obtained from all techniques are in good agreement.

Keywords: Carbon steel; corrosion inhibition; hydrazone derivatives; HCl; quantum chemical calculations

INTRODUCTION

The studies of carbon steel corrosion in acidic media receive more and more attention both of academics and industrials because of the wide applications such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes. Hydrochloric acid is generally used for the removal of undesirable rust in industrial processes. Inhibitors are usually used in these processes to control the corrosion of the metals. Organic compounds containing nitrogen, sulphur oxygen and phosphorous in the conjugated system have particularly been reported as efficient corrosion inhibitors [Nuyuh *et al*, (2002)]. These compounds can adsorb on the steel surface and block the active sites decreasing the corrosion rate. They control corrosion, acting over the anodic or the cathodic surface or both. The selection of a suitable inhibitor for a particular system is a difficult task because of the selectivity of the inhibitors and wide variety of corrosive environment. The choice of the inhibitors was based on the fact that these compounds contain π -electrons and heteroatoms such as N, O, and S which involve greater adsorption of the inhibitor molecules onto the surface of carbon steel. In view of the good performance of hydrazide and thiosemicarbazide-type organic compounds [Mostafa *et al*, (1977)], we have synthesized three novel inhibitors namely methyl 2-(4-hydroxy-4-phenyl but-3-en-2-ylidene) hydrazine carbodithioate (3), methyl 2-(2-hydroxy benzylidene) hydrazine carbodithioate (2) and methyl 2-(4-hydroxy pent-3-en-2-ylidene) hydrazine carbodithioate (1) and have studied their corrosion inhibition properties on carbon steel in 1 M HCl. Chemical (weight loss) and electrochemical techniques (potentiodynamic and ac impedance (EIS)) were used to carry out the measurements. Theoretical calculations based on density functional theory (DFT) were performed, in order to give further insight into the experimental results.

EXPERIMENTAL

Chemicals and Materials

Carbon steel composed of (wt %): 0.200 C, 0.350 Mn, 0.024 P, 0.003 Si and the remainder Fe was used as the working electrode for all studies. Compounds studied in this work have the structures and molecular weights listed in Table (1). Appropriate concentration of acid (HCl 34 %) was prepared by using double-distilled water.

Table (1): Structure and molecular weights of the studied hydrazone derivatives

No.	Name	Structure	Mol.wt.
1	Methyl 2-(4-hydroxy pent-3-en-2-ylidene) hydrazine carbodithioate		204.3
2	Methyl 2-(2-hydroxy benzylidene) hydrazine carbodithioate		226.3
3	Methyl 2-(4-hydroxy-4-phenyl but-3-en-2-ylidene) hydrazine carbodithioate		266.4

METHODS

Chemical technique (weight loss method)

Seven test pieces of carbon steel were cut into 2x1x0.1 cm. They were mechanically polished with emery papers (a coarse paper was used initially and then progressively finer grades were employed), degreased in acetone [Heakel *et al.*, (2011)], rinsed with double distilled water and finally dried between two filter papers and weighed. Weight loss measurements were performed at $30 \pm 1^\circ\text{C}$ for 3 hours by immersing carbon steel pieces into 100 ml acid solution without and with various concentrations of inhibitors. After the elapsed time, the specimen were taken out, washed, dried, and weighed again accurately. The average weight loss at a certain time for each set of the seven samples was taken. The weight loss was recorded to nearest 0.0001 g.

Electrochemical techniques

Potentiodynamic polarization technique

Potentiodynamic measurements were conducted in a conventional three-electrode glass cell of capacity 100 ml, saturated calomel electrode (SCE) and a platinum foil were used as reference and counter electrodes, respectively. The working electrode was carbon steel electrode, which cut from carbon steel sheets with thickness 0.1 cm. The electrode was of dimensions 1 cm x 1 cm and was weld from one side to a copper wire used for electric connection. The sample was embedded in a glass tube using epoxy resin [Fouda *et al.*, (1990)]. A constant quantity of the test solution (100 ml) was taken in the glass cell. The electrode potential was allowed to stabilize for 30 min before starting the measurements. All experiments were conducted at $30 \pm 1^\circ\text{C}$ by using an ultracirculating thermostat. The potentiodynamic current potential curves were recorded by changing the

electrode potential automatically from - 500 to + 500 mV with a scan rate of 5 mV s⁻¹ using an electrochemical measurement system potentiostat / galvanostat / Zera analyzer (Gamry PCI 300/4). This includes Gamry Framework system based on the ESA400, and a personal computer with DC 105 software. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.

Electrochemical impedance spectroscopy technique (EIS)

The cell and the apparatus used in electrochemical impedance spectroscopy (EIS) technique is the same as used in potentiodynamic polarization technique with the same reference, auxiliary and working electrodes. After the determination of steady-state current at a given potential, since wave voltage (5 mV) peak to peak, at frequencies between 100 KHz and 0.1 Hz were superimposed on the rest potential. Gamry applications that include EIS300 for electrochemical impedance spectroscopy along with a computer for collecting data. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. All the potentials reported are referred to SCE. The impedance diagrams are given in the Nyquist and Bode representations.

RESULTS AND DISCUSSION

Weight loss measurements

Weight loss of carbon steel was determined at various time intervals, in the absence and presence of different concentrations of hydrazone derivatives (1-3). Fig. (1) shows the effect of increasing concentration of compound (3), the most effective one, on the weight loss of carbon steel vs. time curves at 30 °C. Similar curves were obtained for other two compounds (not shown). It is obvious that the weight loss of carbon steel in the presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface and, therefore, impede the corrosion process [Otieno-Alego *et al.*, (1992)]. The inhibition efficiency (% IE) and the surface coverage (Θ) that represents the weight of the metal surface covered by inhibitor molecules were calculated using the following equations:

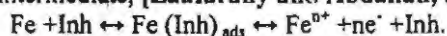
$$\% \text{ IE} = [1 - (W_{\text{inh}} / W_{\text{free}})] \times 100 \quad (1)$$

$$\Theta = [1 - (W_{\text{inh}} / W_{\text{free}})] \quad (2)$$

Where W_{free} and W_{inh} are the weight losses in the absence and presence of inhibitors, respectively. The calculated values of % IE and Θ are listed in table (2) Inspection of table (2) revealed that, the inhibition efficiency increases with an increase in inhibitor concentration. This behavior could be

attributed to increase of the number of adsorbed molecules at metal surface [Sahin *et al.*, (2002)].

The inhibition action of hydrazone derivatives can be explained by considering the following mechanism, $\text{Fe (Inh)}_{\text{ads}}$ is the reaction intermediate, [Zaafarany and Abdallah, (2010)]:



At first, when there is not enough $\text{Fe (Inh)}_{\text{ads}}$ to cover the metal surface, because the inhibitor concentration is low or because the adsorption rate is slow, metal dissolution take place in sites on the carbon steel surface free of $\text{Fe (Inh)}_{\text{ads}}$. With high inhibitor concentration, a compact and coherent inhibitor over film is formed on the carbon steel which reduces chemical attacks on the metal. From data, the % IE has the following order: (3) > (2) > (1).

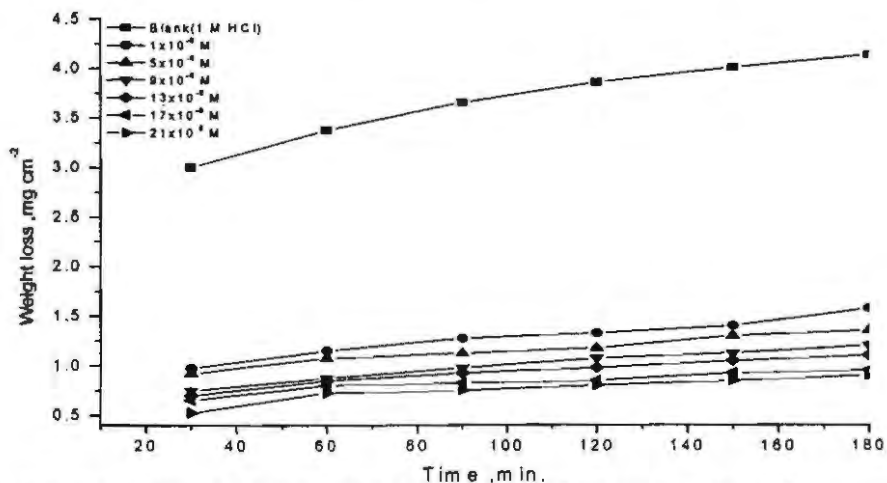


Fig. (1): Weight loss-time curves for the corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of compound (3) at 30 °C.

Table (2): Surface coverage (Θ) and inhibition efficiency (% IE) at different concentrations of inhibitors for the corrosion of carbon steel after 120 min immersion in 1 M HCl at 30 °C.

Conc. μM	Compound (1)		Compound (2)		Compound (3)	
	Θ	% IE	Θ	% IE	Θ	% IE
1	0.143	14.3	0.37	37.0	0.656	65.6
5	0.188	18.8	0.416	41.6	0.695	69.5
9	0.247	24.7	0.424	42.4	0.721	72.1
13	0.448	44.8	0.552	55.2	0.747	74.7
17	0.461	46.1	0.565	56.5	0.780	78.0
21	0.474	47.4	0.571	57.1	0.792	79.2

Electrochemical techniques

Potentiodynamic polarization technique

The kinetics of anodic and cathodic reactions occurring on carbon steel electrodes in 1 M HCl in the absence and presence of different concentrations of hydrazone derivatives was investigated using potentiodynamic polarization technique. The current-potential relationship for the carbon steel electrode at different test solutions of compound (3) is shown in Fig. (2), similar curves were obtained for other two compounds (not shown). Inspection of the Figure revealed that addition of inhibitor causes decrease in the corrosion rate, that is, shifts both the anodic and cathodic curves to lower values of current densities. This implies that both the hydrogen evolution and anodic dissolution reactions of carbon steel electrode corrosion are inhibited. This may be ascribed to adsorption of inhibitor over the corroding surface [Bockris and Drazic, (1962)]. The values of corrosion current densities (j_{corr}), corrosion potential (E_{corr}) / SCE, the cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) obtained from the polarization curves are listed in Table (3). The results in the Table indicated that corrosion current density decreases markedly in the presence of inhibitors compared to the blank solution and also decreases with increasing concentrations of inhibitors. It is also observed that the presence of studied hydrazone derivatives doesn't shift E_{corr} /SCE remarkably; therefore, hydrazone derivatives could be regarded as mixed-type inhibitors and their inhibition on carbon steel occurred by geometric blocking effect mechanism [Mu et al., (2006)]. Both anodic and cathodic Tafel slopes slightly change upon addition of hydrazone derivatives indicates that the inhibitor affects both anodic and cathodic reactions. Corrosion inhibition efficiency was computed using the equation:

$$\% \text{ IE} = [1 - (j_{\text{corr}} / j_{\text{corr}}^{\circ})] \times 100 \quad (3)$$

Where j_{corr} and j_{corr}° are the corrosion current densities in the absence and presence of inhibitors respectively. The values obtained are given in table (3). From this table, it is clear that inhibition efficiency increases with increase in the inhibitor concentration and also the inhibitors have following order according to their inhibition efficiency: (3) > (2) > (1).

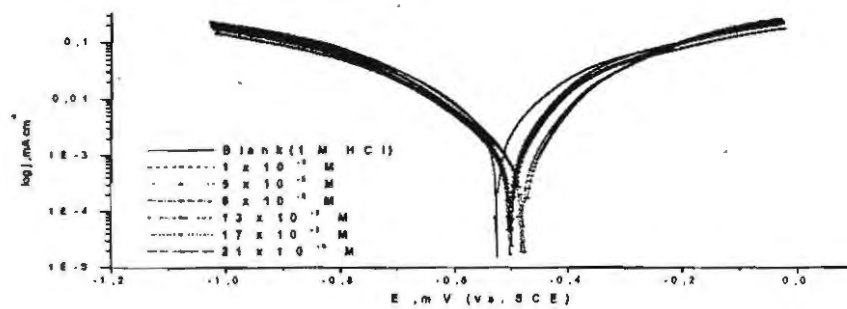


Fig. (2): Potentiodynamic polarization curves for the corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of compound (3) at 30 °C.

Table (3): Potentiodynamic polarization parameters for the corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of inhibitors at 30 °C.

Conc. μM	J_{corr} mA cm^{-2}	$-E_{\text{corr}}$ mV, vs. SCE	β_a mV dec^{-1}	β_c mV dec^{-1}	CR mmy^{-1}	Θ	% IE
Compound (1)							
Blank	2.81	483	205	226	1088.0	—	—
1	1.907	488	175	206	845.5	0.224	22.4
5	1.869	496	176	212	782.0	0.281	28.1
9	1.724	515	124	156	753.7	0.309	30.9
13	1.463	510	115	158	745.4	0.366	36.6
17	1.192	510	169	182	705.7	0.427	42.7
21	1.185	510	88	140	674.4	0.541	54.1
Compound (2)							
1	1.907	480	157	194	739.7	0.321	32.1
5	1.869	495	157	194	724.7	0.334	33.4
9	1.724	515	110	141	668.5	0.386	38.6
13	1.463	484	154	201	567.3	0.479	47.9
17	1.192	495	120	157	462.1	0.575	57.5
21	1.185	481	113	147	459.5	0.578	57.8
Compound (3)							
1	1.112	482	112	144	431.3	0.604	60.4
5	0.9243	478	112	168	359.5	0.671	67.1
9	0.9138	501	84	120	354.4	0.674	67.4
13	0.8689	500	80	127	337.0	0.690	69.0
17	0.7854	505	71	104	305.6	0.720	72.0
21	0.5374	503	57	83	208.4	0.808	80.8

Electrochemical impedance spectroscopy technique (EIS)

Impedance diagrams (Nyquist and Bode) at frequencies ranging from 100 KHz to 0.1 Hz for carbon steel in inhibitor free and inhibitor containing 1 M HCl solution were traced at the stabilized E_{oc} value. The equivalent circuit model which describes the metal / electrolyte interface of the present corroding system is shown as insert in Fig. (3), where R_s , R_{ct} and CPE refer to solution resistance, charge transfer resistance and constant phase element representing the double layer capacitance (C_d) of the interface, respectively. A typical example of EIS data obtained for compound (3) is represented as Nyquist and Bode plots in Fig. (4a and 4b), similar curves were obtained for the other two compounds (not shown). The complex impedance diagram is characterized by a single full semicircular appearance indicating that corrosion of carbon steel is controlled by a charge transfer process [Li *et al.*,

(2009)]. Small distortion was observed in the diagrams, this distortion has been attributed to frequency dispersion [Solmaz *et al.*, (2008)]. The obtained diameters of the capacitive loops increase in presence of hydrazone derivatives, and are indicative of the extent of inhibition of corrosion process, contrary to the decrease of the capacity of double layer (C_{dl}) which is defined as:

$$C_{dl} = (2 \pi f_{max} R_{ct})^{-1} \quad (4)$$

The inhibition efficiencies obtained from the EIS measurements are calculated from the relation:

$$\% IE = [1 - (R_{ct} / R'_{ct})] \times 100 \quad (5)$$

Where R_{ct} and R'_{ct} are the transfer resistance without and with the inhibitor, respectively. The analysis of the EIS parameters shows that R_{ct} increases by increasing the concentration of hydrazone derivatives, giving consequently a decrease in the corrosion rate. It is important to emphasize that the values of C_{dl} with increasing the inhibitor concentration. This is due to the gradual replacement of water molecules in the double layer by the adsorbed inhibitor molecules which form on adherent film on the metal surface and leads to decrease in the local dielectric constant of the metal solution interface [Fouda *et al.*, (2009)]. The obtained Bode plot for compound (3) is shown in Fig. (4b). The high frequency limits corresponds to ($R_{ct} + R_s$). The low frequency contribution shows the kinetic response of charge transfer reaction [Fouda *et al.*, (2005)]. EIS data are shown in table (4), from this table, it is clear that the studied compounds have the same order obtained from the other techniques according to their inhibition efficiencies [$3 > 2 > 1$]. It can be concluded that the inhibition efficiency from weight loss, polarization curves, electrochemical impedance spectroscopy measurements are in good agreement.

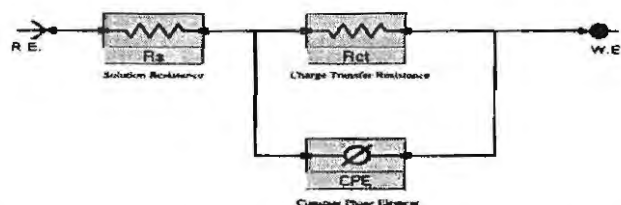


Fig. (3): Equivalent circuit model used to fit experimental EIS data recorded for carbon steel electrode in 1 M HCl.

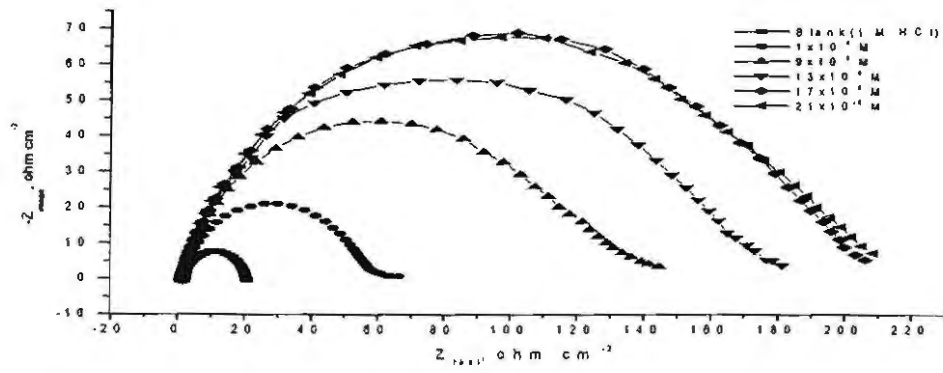


Fig. (4a) Nyquist plot for the corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of compound (3) at 30 °C.

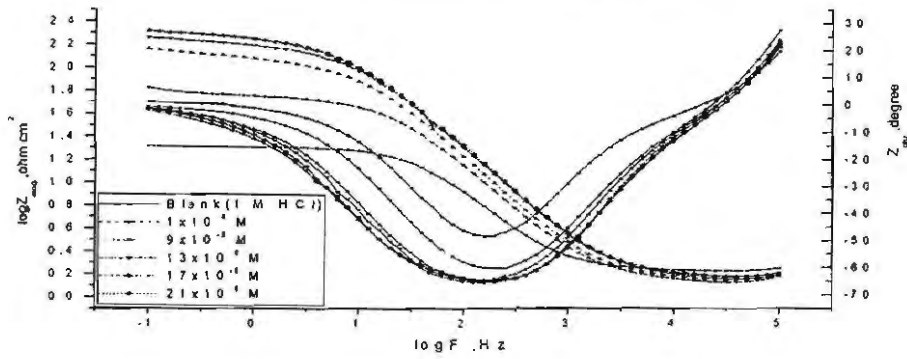


Fig. (4b): Bode plot for the corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of compound (3) at 30 °C.

Table (4): EIS parameters for the corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of inhibitors at 30 °C.

Conc. μM	C _d μF cm ⁻²	R _{ct} Ω cm ²	θ	% IE
Compound (1)				
Blank	2.11	18.76	---	---
1	1.92	25.33	0.259	25.9
9	1.73	28.61	0.344	34.4
13	1.37	32.16	0.416	41.6
17	1.33	40.51	0.536	53.6
21	1.32	47.15	0.602	60.2
Compound (2)				
1	1.73	27.5	0.317	31.7
9	1.72	31.34	0.401	40.1
13	1.55	37.61	0.501	50.1
17	1.34	40.57	0.537	53.7
21	1.29	50.61	0.629	62.9
Compound (3)				
1	1.40	56.49	0.667	66.7
9	1.36	125.3	0.850	85.0
13	1.19	164.4	0.885	88.5
17	1.18	189.5	0.901	90.1
21	1.02	190.6	0.902	90.2

Adsorption isotherm behavior

The adsorption on the corroding surfaces never reaches the real equilibrium and tends to reach an adsorption steady state. When corrosion rate is sufficiently decreased in the presence of inhibitor, the adsorption steady state has a tendency to attain quasi-equilibrium adsorption in thermodynamic was using the appropriate adsorption isotherm. The degree of surface coverage (Θ) was obtained from average weight loss data and it was found to increase with increasing the concentration of the additives, and decreases with rise in temperature from 30 to 60 °C Table (5). Various adsorption isotherms were tested to find the best suitable adsorption isotherm for adsorption of the studied hydrazone derivatives on the surface of carbon steel from 1 M HCl solution. Temkin adsorption isotherm was found to fit the experimental data. Temkin mathematical expression is given as follows [Finley and Hackerman, (1960)]:

$$\Theta = \frac{1}{f} \ln K_{ads} + \frac{1}{f} \ln C_{inh} \quad (6)$$

Where C_{inh} is the inhibitor bulk concentration in (M), K_{ads} (M^{-1}) is the equilibrium constant of adsorption and f is the Temkin heterogeneity factor which is related to Frumkin lateral interaction factor a ($f = -2a$). a is the factor that describe the molecular interactions in the adsorbed layer. From the

intercepts of the straight lines on the Θ -axis (Fig. (5) for compound 3 for example), K_{ads} can be calculated.

Also, some thermodynamic adsorption parameters were computed. The well known thermodynamic adsorption parameters are the free energy of adsorption (ΔG_{ads}°), the heat of adsorption (ΔH_{ads}°) and the entropy of adsorption (ΔS_{ads}°). These quantities can be calculated by various mathematical methods depending on the estimated values of K_{ads} from adsorption isotherms at different temperatures. It is well known that K_{ads} represents the strength between adsorbate and adsorbent. Large values of K_{ads} imply more efficient adsorption and hence better inhibition efficiency [Durnie et al, (1999)]. The ΔG_{ads}° values at all studied temperatures can be calculated from the following equation [Lebrini et al, (2005)]:

$$K_{ads} = (1/55.5) \exp(-\Delta G_{ads}^{\circ}/RT) \quad (7)$$

where 55.5 is the concentration of water in mol l⁻¹. The heat of adsorption (ΔH_{ads}°) could be calculated according to the Van't Hoff equation [Bentiss et al, (2005)]:

$$\log K_{ads} = (-\Delta H_{ads}^{\circ}/2.303RT) + \text{constant} \quad (8)$$

In order to calculate heat of adsorption (ΔH_{ads}°), $\log K_{ads}$ was plotted against $1/T$ as shown in Fig. (6). The straight lines were obtained with slope equal to $(-\Delta H_{ads}^{\circ}/2.303R)$. Then in accordance with the basic equation:

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \quad (9)$$

By introducing the obtained ΔG_{ads}° and ΔH_{ads}° values in equation (9), the entropy of adsorption (ΔS_{ads}°) values were calculated at all studied temperatures. All estimated thermodynamic adsorption parameters for studied hydrazone derivatives on carbon steel from 1 M HCl solution were listed in table (6). From the data recorded in table (6) it can be concluded that:

- i) The experimental data give good curves fitting for the applied adsorption isotherms as the correlation coefficients (R^2) were in the range 0.980-0.997.
- ii) K_{ads} value decreases with temperature from 30 to 60 °C.
- iii) The negative values of ΔG_{ads}° reflect that the adsorption of studied hydrazone derivatives on carbon steel surface from 1 M HCl solution is spontaneous process [Noor, (2007)].
- iii) ΔG_{ads}° may increases (becomes less negative) with an increase of temperature which indicates the occurrence of exothermic process at which adsorption was unfavorable with increasing reaction temperature as the result of the inhibitor desorption from the steel surface [Mousa et al, (2009)].
- iv) It is usually accepted that the value of ΔG_{ads}° around -20 kJ mol⁻¹ or lower indicates the electrostatic interaction between charged metal surface and charged organic molecules in the bulk of the solution while those around -40 kJ mol⁻¹ or higher involve charge sharing or charge transfer between the metal surface and organic molecules [Li and Mu, (2005)]. From the obtained values of ΔG_{ads}° it was found that the existence of comprehensive adsorption (physical and chemical adsorption), that is to say, since the adsorption heat

approached the general chemical reaction heat, the chemical adsorption occur.

- v) The negative sign of ΔH_{ads}° reveals that the adsorption of inhibitor molecules is an exothermic process. Generally, an exothermic adsorption process suggests either physisorption or chemisorption while endothermic process is attributed to chemisorption [Abd El-Rehim *et al.*, (2001)]. In an exothermic process, physisorption is compared to chemisorption by considering the absolute value of adsorption enthalpy. Generally, enthalpy values up to 41.9 kJ mol^{-1} are related to the electrostatic interactions between charged molecules and charged metal (physisorption) while those around 100 kJ mol^{-1} or higher are attributed to chemisorption. The unshared electron pairs in investigated molecules may interact with d-orbitals of carbon steel to provide a protective chemisorbed film [Tang *et al.*, (2006)]. In the case of investigated compounds, the absolute values of enthalpy are relatively high, approaching those typical of chemisorption. The values of ΔS_{ads}° in the presence of investigated compounds are large and negative that is accompanied with exothermic adsorption process [Mu *et al.*, (2005)].

Activation energy calculations

In order to study the effect of temperature on the inhibition characteristic of all the studied hydrazone derivatives, weight loss measurements were performed at different temperatures from 30 to 60 °C in the absence and presence of different concentrations of the studied hydrazone derivatives for 3 h immersion time. As noticed previously, the adsorption process was well elucidating by using a thermodynamic model, in addition a kinetic thermodynamic model was another tool to explain the mechanism of corrosion inhibition for an inhibitor.

The apparent effective activation energies (E_a^*) for the corrosion reaction of carbon steel in 1 M HCl solution and presence of different concentrations of inhibitors were calculated from Arrhenius type equation [Moretti *et al.*, (1996)]:

$$\log k_{corr} = \log A - E_a^* / (2.303RT) \quad (10)$$

Where A is the Arrhenius pre-exponential factor. A plot of $\log k_{corr}$ versus $1/T$ gave straight lines as shown in fig. (6). The enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) were obtained by applying the transition-state equation [Solomon *et al.*, (2010)]:

$$\log(k_{corr}/T) = [\log(R/Nh) + (\Delta S^* / 2.303R) - (\Delta H^* / 2.303RT)] \quad (11)$$

From which the values of ΔH^* and ΔS^* were calculated, respectively Fig. (7). All estimated thermodynamic - kinetic parameters were tabulated in table (7). The obtained data in Table (7) can be interpreted as follows:

- i) In 1.0 M HCl solutions, the addition of the studied hydrazone derivatives lead to an increase in the apparent activation energy to values greater than that of the uninhibited solution suggesting that higher energy barrier for the corrosion process in the inhibited solutions associated with physical

adsorption or weak chemical bonding between the inhibitor species and the steel surface [Ebenso, (2003)].

ii) All values of E_a^* are larger than the analogous values of ΔH^* indicating that the corrosion process must involved a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume [Laidler, (1963)].

iii) The entropy of activation (ΔS^*) in the absence and presence of inhibitor has negative values, this indicates that the activated complex in the rate determining step represents an association rather than dissociation, meaning that, a decrease in disordering takes place on going from reactants to the activated complex [Gomma and Wahdan, (1995)].

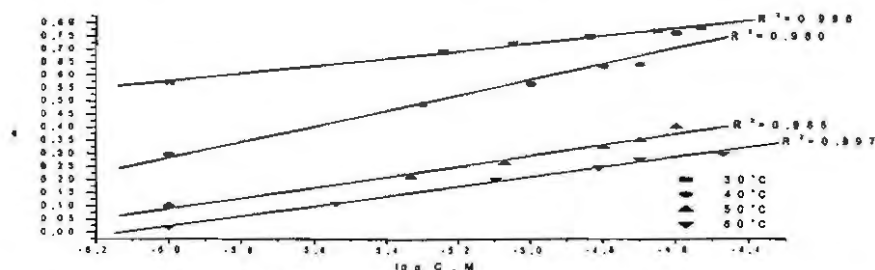


Fig. (5): Temkin adsorption isotherm of compound (3) on carbon steel surface in 1 M HCl at different temperatures.

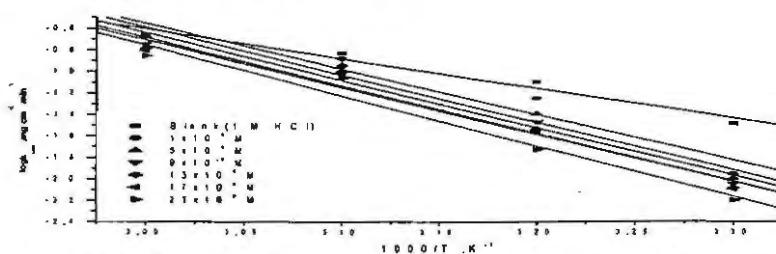


Fig. (6): Arrhenius plot for carbon steel corrosion rates (k_{corr}) after 120 min immersion in 1 M HCl in the absence and presence of various concentrations of compound (3).

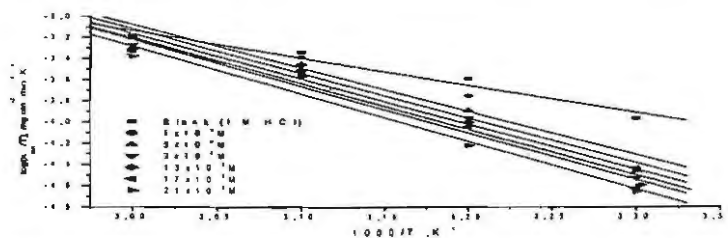


Fig. (7): Transition state plot for carbon steel corrosion rates (k_{corr}) in the absence and presence of various concentrations of compound (3).

Table (5): Variation of inhibition efficiencies (% IE) and surface coverage (Θ) for various concentrations of the studied inhibitors at different temperatures.

Temp. °C	Conc. μM	Compound (1)		Compound (2)		Compound (3)	
		Θ	% IE	Θ	% IE	Θ	% IE
30	1	0.143	14.3	0.370	37.0	0.656	65.6
	5	0.188	18.8	0.416	41.6	0.695	69.5
	9	0.247	24.7	0.424	42.4	0.721	72.1
	13	0.448	44.8	0.552	55.2	0.747	74.7
	17	0.461	46.1	0.565	56.5	0.780	78.0
	21	0.474	47.4	0.571	57.1	0.792	79.2
40	1	0.092	9.2	0.131	13.1	0.295	29.5
	5	0.271	27.1	0.316	31.6	0.490	49.0
	9	0.335	33.5	0.372	37.2	0.567	56.7
	13	0.350	35.0	0.408	40.8	0.635	63.5
	17	0.379	37.9	0.414	41.4	0.641	64.1
	21	0.406	40.6	0.474	47.4	0.762	76.2
50	1	0.065	6.5	0.739	7.4	0.102	10.2
	5	0.152	15.2	0.162	16.2	0.210	21.0
	9	0.179	17.9	0.186	18.6	0.238	23.8
	13	0.206	20.6	0.223	22.3	0.325	32.5
	17	0.210	21.0	0.207	20.7	0.352	35.2
	21	0.250	25.0	0.186	18.6	0.403	40.3
60	1	0.004	0.4	0.011	1.1	0.020	2.0
	5	0.005	0.5	0.025	2.5	0.033	3.3
	9	0.027	2.7	0.140	14.0	0.171	17.1
	13	0.047	4.7	0.167	16.7	0.250	25.0
	17	0.067	6.7	0.182	18.2	0.279	27.9
	21	0.091	9.1	0.205	20.5	0.352	35.2

Table (6): Thermodynamic parameters for the adsorption of inhibitors on carbon steel surface in 1 M HCl at different temperatures.

Temp. °C	$K_{\text{ads}} \times 10^{-6}$ M^{-1}	$-\Delta G^{\circ}_{\text{ads}}$ kJ mol^{-1}	$-\Delta H^{\circ}_{\text{ads}}$ kJ mol^{-1}	$-\Delta S^{\circ}_{\text{ads}}$ $\text{J mol}^{-1} \text{K}^{-1}$
Compound (1)				
30	9.0769	50.5	102.4	0.171
40	2.9387	49.2	102.4	0.169
50	1.5984	49.0	102.4	0.165
60	0.2053	44.9	102.4	0.173
Compound (2)				
30	338.3	59.5	158.7	0.327
40	4.3	50.2	158.7	0.347
50	2.3	50.0	158.7	0.337
60	1.0	49.4	158.7	0.328
Compound (3)				
30	8973.4	67.8	255.0	0.618
40	8.7	52.0	255.0	0.649
50	2.7	50.6	255.0	0.633
60	1.3	50.1	255.0	0.615

Table (7): Kinetic-thermodynamic parameters for carbon steel corrosion in the absence and presence of various concentrations of inhibitors.

Conc. μM	$A \times 10^{-12}$ $\text{g cm}^{-2} \text{min}^{-1}$	E_p kJ mol^{-1}	ΔH^\ddagger kJ mol^{-1}	$-\Delta S^\ddagger$ $\text{J mol}^{-1} \text{K}^{-1}$
Compound (1)				
Blank	47.2	52.8	49.6	108.8
1	185.8	56.7	53.9	95.7
5	427.6	59.2	56.6	88.3
9	779.8	60.9	57.8	84.8
13	9682.8	67.8	65.3	62.1
17	10115.8	68.0	66.1	60.0
21	9772.4	68.0	66.7	58.3
Compound (2)				
1	2.9	64.1	61.9	71.3
5	6.6	66.6	63.9	65.9
9	7.4	67.2	64.7	64.4
13	17.4	69.6	67.4	56.4
17	18.6	69.9	68.8	52.4
21	17.6	70.0	69.4	51.2
Compound (3)				
1	1.5	81.2	78.7	20.4
5	4.7	84.6	80.9	14.3
9	4.1	84.6	81.9	12.3
13	4.3	85.0	82.8	10.5
17	5.2	85.7	84.4	5.9
21	20.5	89.8	85.9	2.5

Chemical quantum calculations

Several attempts have been made to predict corrosion inhibition efficiency using a number of individual parameters obtained through quantum chemical calculation method. These trials were aimed to find possible correlations between corrosion inhibition efficiency and some quantum molecular properties such as dipole moment (μ), energies of the highest occupied molecular orbital (E_{HOMO}), the lowest unoccupied molecular orbital (E_{LUMO}) and the difference between them [$\Delta E = (E_{\text{LUMO}} - E_{\text{HOMO}})$ energy gap] [Bouklan *et al.*, (2010)]. E_{HOMO} is often associated with the electron donating ability of the molecules. High values of E_{HOMO} are likely to indicate the tendency of the molecule to donate electrons to appropriate acceptor molecules with lower energy molecular orbitals (MO). E_{LUMO} , on the other hand, indicates the ability of the molecules to accept electrons [Lazarova *et al.*, (2010)]. The binding ability of the inhibitor to the metal surface increases with increasing E_{HOMO} and decreasing E_{LUMO} energy values. Thus, the lower the value of (E_{LUMO}), the most probable it is that the molecule would accept electrons. Moreover, the gap between the E_{LUMO} and E_{HOMO} energy levels of the molecules is important parameters that determine

the reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE decreases the reactivity of the molecules increases leading to increase in the inhibition efficiency of the molecule [Shorky *et al.*, (1998)]. From this **fig. (8)**, it could be seen that these compounds have different E_{HOMO} and E_{LUMO} distributions in the neutral form. The HOMO densities were concentrated on both N and S atoms. For the LUMO distributions, the reverse is the case. Thus, unoccupied d orbitals of Fe atom can accept electrons from inhibitor molecules mainly in the neutral form to form a coordinate bond. Also, the inhibitor molecule can accept electrons from Fe atom with its antibonding orbitals to form back-donating bond. These donation and back-donation processes strengthen the adsorption of inhibitors onto the carbon steel surface [Lebrini *et al.*, (2005)]. Also the less negative HOMO and the smaller energy gap are reflected the stronger chemisorptions bond and perhaps greater inhibitor efficiency [Lazarova *et al.*, (2010)]. Values of (E_{HOMO}), (E_{LUMO}) and ΔE are given in **table (8)**. In accordance with data obtained from chemical quantum calculations, the studied inhibitors have the same order obtained from experimental techniques according to their inhibition efficiency, (3) > (2) > (1).

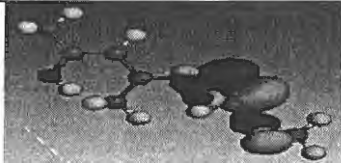

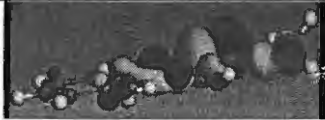
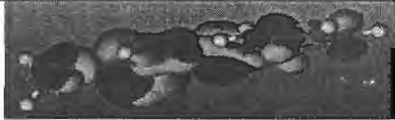
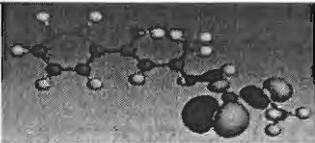

Comp.	HOMO	LUMO
1		
2		
3		

Fig. (8): Optimized molecular structure of hydrazone derivatives.

Table (8): Quantum chemical calculations for the studied hydrazone derivatives

Inhibitors	$-E_{\text{HOMO}}$ eV	$-E_{\text{LUMO}}$ eV	$-\Delta E$ eV	μ Debye
Compound (1)	8.839	1.336	7.503	2.844
Compound (2)	8.835	1.366	7.469	2.827
Compound (3)	8.812	1.378	7.434	2.838

Mechanism of inhibition

From the results obtained using electrochemical and weight loss measurements, it was concluded that all the three hydrazone derivatives inhibit the corrosion of carbon steel in 1.0 M HCl by adsorption at carbon steel/solution interface. It is general assumption that the adsorption of organic inhibitors at the metal surface interface is the first step in the mechanism of the inhibition action. Organic molecules may be adsorbed on the metal surface in four types, namely: 1) Electrostatic interaction between the charged molecules and the charged metal, 2) Interaction of unshared electron pairs in the molecule with the metal, 3) Interaction of π - electrons with the metal and 4) A combination of the above [Singh and Quraishi, (2009)].

The inhibition of active dissolution of the metal is due to the adsorption of the inhibitor molecules on the metal surface forming a protective film. The inhibitor molecules can be adsorbed onto the metal surface through electron transfer from the adsorbed species to the vacant electron orbital of low energy in the metal to form a co-ordinate link. The inhibition efficiency depends on many factors [Bentiss *et al.*, (2009)] including the number of adsorption centers, mode of interactions with metal surface, molecular size and structure. It is well known that iron has co-ordination affinity toward nitrogen, sulfur and oxygen-bearing ligands [Synder *et al.*, (1989)]. Hence, adsorption on iron can be attributed to co-ordination through hetero atoms (N, S and O) and π - electrons of aromatic ring. The inhibition efficiency of the studied inhibitors was decreased according to the following order: (3) > (2) > (1).

The inhibition effect of HD (hydrazone derivatives) in HCl solution can be explained as follows: $\text{HD} + x\text{H}^+ \rightarrow [\text{HDH}_x]^{x+}$

The inhibitor interacts with carbon steel surface via protonated group, adsorbed at cathodic sites and hinders the hydrogen evolution reaction. In other hand, HD may adsorb at anodic sites on metal surface via chemisorption mechanism, by sharing electrons of S, N and O atoms and also by donor acceptor interactions between π -electrons of phenyl ring and vacant d-orbital of iron [Lece *et al.*, (2008)].



Hence by following above mechanism, HD molecules have ability to influence both cathodic and anodic reactions giving rise to mixed inhibition mechanism.

The results show that among the investigated compounds inhibitor (3) exhibits the best performance because of the presence of highly electron releasing methyl group (with Hammett constant $\sigma = -0.17$) [Hammett, (1940)] and the higher molecular size (266.4) as the adsorbed species cover a wide area of the corroded metal and protect it. The $-\text{CH}_3$ group increases the electron density on the active centers, which leads to greater surface coverage, thereby giving higher inhibition efficiency. Compound (2) has the same number of active sites (S, N, O atoms) as compound (3) with the replacement of methyl group by H atom. So, compound (2) comes next to compound (3) in the order of % inhibition and also, due to its lower molecular size than compound (III) (226.3). Compound (1) is the least effective one; in spite of it has the same number of active sites (S, N, and O atoms). This is due to: i) the absence of benzene ring which provides π -electrons to the molecules and ii) its lower molecular size than compounds (2 and 3).

CONCLUSIONS

- 1) In 1.0 M HCl, the inhibition efficiency of hydrazone derivatives increases with increasing concentration and decreases with rise in temperature.
- 2) The inhibition action of hydrazone derivatives is performed via adsorption of the hydrazone derivatives on carbon steel surface. The adsorption is spontaneous and follows Temkin adsorption isotherm at all studied temperatures.
- 3) Thermodynamic data led to suggest the occurrence of comprehensive adsorption (physical and chemical adsorption).
- 4) The results obtained from DC, AC and weight loss measurements are in good agreement and they in accord also with the theoretical calculated values of E_{HOMO} and E_{LUMO} of the investigated compounds.
- 5) The inhibition efficiency of the investigated inhibitors is as the following order: (3) > (2) > (1).

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الملخص العربي

مشتقات الهيدرازون كمثبطات لتآكل الصلب الكربوني في محاليل حمض الهيدروكلوريك

أ. د. عبد العزيز السيد فوده و داليا محمد صبح

تم استخدام بعض مشتقات الهيدرازون كمثبطات لتآكل الصلب الكربوني في 1 مولر من حمض الهيدروكلوريك بطرق كيميائية (فقد الوزن) وكهروكيميائية (الاستقطاب البوتشوديناميكي والمعاقه الكهروكيميائية). وجد من النتائج ان كفاءة التثبيط تعتمد على تركيز هذه المركبات والتركيب الكيميائي لها. وقد دلت طريقة الاستقطاب البوتشوديناميكي على ان هذه المركبات تعمل كمثبطات مختطه (انودية وكاثودية) وان ادمصاص هذه المركبات على سطح الصلب الكربوني يتبع ايزوترم تمكن.

