

Dry and Wet Lab Studies for Some 3-Carbohydrazone Derivatives as Possible Corrosion Inhibitors for C-Steel in 2 M HCl

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Abstract—With contrast to the traditional techniques of identifying new corrosion inhibitors in wet lab, a prior dry-lab process, followed by a wet-lab process is suggested by using cheminformatics tools. Quantum chemical method is used to explore the relationship between the inhibitor molecular properties and its inhibition efficiency. The density function theory (DFT) is also used to study the structural properties of four selected 3-carbohydrazone derivatives in aqueous phase. It is found that when the 3-carbohydrazone derivatives adsorb on the C-steel surface, molecular structure influences their interaction mechanism. The inhibition efficiencies of these compounds showed a certain relationship to highest occupied molecular orbital (HOMO) energy, Mulliken atomic charges and Fukui indices. A wet lab study has been carried out using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Electrochemical frequency modulation (EFM) measurements to evaluate their inhibition performance in 2 M HCl solutions at 25° C. Adsorption takes place by a direct chemisorption on the exposed copper surface, while it most probably occurs via hydrogen bonding on the oxidized surface. Compound (3) was the most effective among the four tested inhibitors, while Compound (1) was less effective than Compound (3). Results obtained from dry-lab process are in good agreement with those recorded from wet-lab experiments.

Keywords— Wet-Lab Experiments, C-Steel, HCl, EFM, EIS.

I. INTRODUCTION

C-Steel has been extensively used under different conditions in petroleum industries [1]. Aqueous solutions of acids are among the most corrosive media and are widely used in industries for pickling, acid cleaning of boilers, descaling and oil well [2, 6]. The main problem concerning C-

steel applications is its relatively low corrosion resistance in acidic solution.

Several methods used currently to reduce corrosion of C-steel. One of such methods is the use of organic inhibitors [7-17]. Effective inhibitors are heterocyclic compounds that have π bonds, heteroatoms such as sulphur, oxygen and nitrogen [18]. Compounds containing both nitrogen and chloro atoms can provide excellent inhibition, compared with compounds containing only nitrogen or chloro atom [19]. Heterocyclic compounds such as 3-carbohydrazone derivatives can provide excellent inhibition. These molecules depends mainly on certain physical properties of the inhibitor molecules such as functional groups, steric factors, electron density at the donor atom and electronic structure of the molecules [20, 21]. Regarding the adsorption of the inhibitor on the metal surface, two types of interactions are responsible. One is physical adsorption which involves electrostatic force between ionic charges or dipoles of the adsorbed species and electric charge at metal/ solution interface. Other is chemical adsorption, which involves charge sharing or charge transfer from inhibitor molecules to the metal surface to form coordinated types of bonds [22]. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, and temperature.

The purpose of this paper is to compare the corrosion inhibition data derived from EFM with that obtained from Tafel extrapolation and EIS techniques. It was also the purpose of the present work to discuss the relationship between quantum chemical calculations and experimental protection efficiencies of the tested 3-carbohydrazone derivatives by determining various quantum chemical parameters. These parameters include the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO} .

II. EXPERIMENTAL DETAILS

Composition of Material Samples

TABLE I
CHEMICAL COMPOSITION (WEIGHT %) OF THE CARBON STEEL

Element	C	Mn	P	Si	Fe
Weight (%)	0.200	0.350	0.024	0.003	rest

Chemicals and Solutions

Hydrochloric acid (37%), ethyl alcohol and acetone were purchased from Al-gomhoria Company. Bidistilled water was used throughout all the experiments.

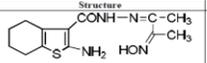
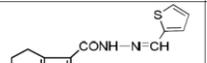
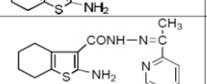
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TABLE II
MOLECULAR STRUCTURES, FORMULAS AND MOLECULAR WEIGHTS OF THE
INVESTIGATED 3-CARBOHYDRAZIDE DERIVATIVES [23].

Cpd	Structure	Name	Chemical Formula	M.Wt
1		Ammono-N-(3-(4-(di-oxycycano) butan-2-ylidene)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbohydrazide	C ₁₁ H ₁₆ N ₂ O ₂ S	294.37
2		Ammono-N-(thiophen-2-ylmethylene)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbohydrazide	C ₁₄ H ₁₂ N ₂ O ₂ S	305.42
3		Ammono-N-(1-(pyridin-2-yl) ethylidene)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbohydrazide	C ₁₆ H ₁₄ N ₂ O ₂ S	341.41

Electrochemical Measurements

The experiments were carried out potentiodynamically in a thermostated three electrode cell. Platinum foil was used as counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. The working electrode was in the form of a square cut from C-steel under investigation and was embedded in a Teflon rod with an exposed area of 1 cm². This electrode was immersed in 100 ml of a test solution for 30 min until a steady state open-circuit potential (E_{ocp}) was attained. Potentiodynamic polarization was conducted in an electrochemical system (Gamry framework instruments version 3.20) which comprises a PCI/300 potentiostat, controlled by a computer recorded and stored the data. The potentiodynamic curves were recorded by changing the electrode potential from -1.0 to 0.0 V versus SCE with scan rate of 5 mV/s. All experiments were carried out in freshly prepared solution at constant temperature (25 ± 1 °C) using a thermostat. IE% and the degree of surface coverage (θ) were defined as:

$$\%IE = \theta \times 100 = [(i_{\text{corr}} - i_{\text{corr(inh)}}) / i_{\text{corr}}] \times 100 \quad (1)$$

Where i_{corr} and $i_{\text{corr(inh)}}$ are the uninhibited and inhibited corrosion current density values, respectively, determined by extrapolation of Tafel lines.

The electrochemical impedance spectroscopy (EIS) spectra were recorded at open circuit potential (OCP) after immersion the electrode for 15 min in the test solution. The ac signal was 5 mV peak to peak and the frequency range studied was between 100 kHz and 0.2 Hz. All Electrochemical impedance experiments were carried out using Potentiostat/Galvanostat/Zra analyzer (Gamry PCI 300/4). A personal computer with EIS300 software and Echem Analyst 5.21 was used for data fitting and calculating.

The inhibition efficiency (% IE) and the surface coverage (θ) of the used inhibitors obtained from the impedance measurements were calculated by applying the following relations:

$$\%IE = \theta \times 100 = [1 - (R_{\text{ct}}^{\circ} / R_{\text{ct}})] \quad (2)$$

Where, R_{ct}° and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively.

EFM experiments were performed with applying potential perturbation signal with amplitude 10 mV with two sine waves of 2 and 5 Hz. The choice for the frequencies of 2 and 5Hz were based on three arguments [24]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors CF2 and CF3 [25].

All electrochemical experiments were carried out using Gamry instrument PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 Corrosion software, EIS300 Electrochemical Impedance Spectroscopy software, EFM140 Electrochemical Frequency Modulation software and Echem Analyst 5.5 for results plotting, graphing, data fitting and calculating.

Theoretical Study

Accelrys (Material Studio Version 4.4) software for quantum chemical calculations has been used.

III. RESULTS AND DISCUSSION

A. Potentiodynamic Polarization Measurements

Fig. (1) shows the potentiodynamic polarization curves for C-steel without and with different concentrations of compound (1). Similar curves for other compounds were obtained and are not shown at 25 °C. The obtained electrochemical parameters; cathodic (β_c) and anodic (β_a) Tafel slopes, corrosion potential (E_{corr}), and corrosion current density (i_{corr}), were obtained and listed in Table. (3) which shows that i_{corr} decreases by adding the 3-carbohydrazide compounds and by increasing their concentration. In addition, E_{corr} does not change obviously. Also β_a and β_c do not change markedly, which indicates that the mechanism of the corrosion reaction of C-steel does not change. Fig. (1) clearly shows that both anodic and cathodic reactions are inhibited, which indicates that investigated compounds act as mixed-type inhibitors [26-27]. The inhibition achieved by these compounds decreases in the following order: Compound (3) > Compound (2) > Compound (1).

Also, the results of θ and % IE where calculated using i_{corr} values. The percentage inhibition efficiencies (% IE) calculated from i_{corr} of the investigated compounds are given in Table (3). An inspection of the results obtained from this Table reveals that, the presence of different concentrations of the additives reduces the anodic and cathodic current densities and the polarization resistance. This indicates that the inhibiting effects of the investigated compounds. The order of decreasing inhibition efficiency from i_{corr} is: Compound (3) > Compound(2) > Compound(1).

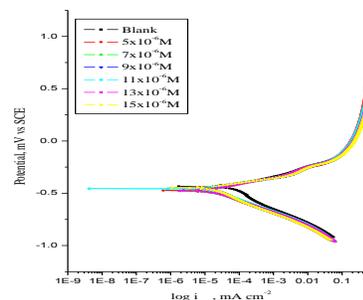


Fig. 1 Potentiodynamic Polarization Curves for the Corrosion of C-Steel in 2 M HCl in the Absence and Presence of Various Concentrations of Compound (1) at 25°C.

TABLE III

EFFECT OF CONCENTRATIONS OF THE INVESTIGATED COMPOUNDS ON THE FREE CORROSION POTENTIAL (E_{CORR}), CORROSION CURRENT DENSITY (i_{CORR}), TAFEL SLOPES (β_a & β_c), DEGREE OF SURFACE COVERAGE (Θ) AND INHIBITION EFFICIENCY (%IE) FOR C-STEEL IN 2 M HCL AT 25°C.

Cpd	Conc., M	$-E_{\text{corr}}$, mV (vs SCE)	i_{corr} , $\mu\text{A cm}^{-2}$	β_a , mV dec $^{-1}$	β_c , mV dec $^{-1}$	Θ	% IE
(1)	Blank	480	9.91	101.5	148.5	----	----
	5×10^{-6}	466	8.85	67.9	127.5	0.106	10.6
	7×10^{-6}	479	8.84	74.0	128.2	0.108	10.8
	9×10^{-6}	454	8.78	64.8	136.0	0.114	11.4
	11×10^{-6}	466	8.60	87.3	162.5	0.132	13.2
	13×10^{-6}	479	8.46	71.5	125.3	0.146	14.6
(2)	15×10^{-6}	466	8.38	82.9	186.3	0.154	15.4
	5×10^{-6}	466	8.25	81.7	184.3	0.167	16.7
	7×10^{-6}	466	8.15	87.7	196.0	0.178	17.8
	9×10^{-6}	466	8.00	87.3	162.5	0.192	19.2
	11×10^{-6}	466	7.87	80.4	187.7	0.206	20.6
	13×10^{-6}	466	7.54	64.4	125.3	0.238	23.8
(3)	15×10^{-6}	477	6.70	84.2	132.5	0.323	32.3
	5×10^{-6}	466	6.08	73.2	144.9	0.386	38.6
	7×10^{-6}	460	6.03	73.5	144.0	0.392	39.2
	9×10^{-6}	439	5.90	70.9	183.9	0.405	40.5
	11×10^{-6}	439	5.76	67.4	169.9	0.417	41.7
	13×10^{-6}	467	4.95	87.9	157.3	0.496	49.6
	15×10^{-6}	453	4.62	63.6	134.7	0.514	51.4

A.2. Adsorption Isotherm

The adsorption isotherms are considered to describe the interactions of the inhibitor molecule with the active sites on the metal surface [28]. Attempts were made to fit Θ values to various isotherms including Frumkin, Langmuir, Temkin, and Freundlich. The results were best fitted by far by the Langmuir adsorption isotherm which has the following equation [29-30]:

$$C/\Theta = 1/K_{\text{ads}} + C \quad (3)$$

Where C is the concentration of 3-carbohydrazide; K_{ads} is the adsorptive equilibrium constant; and Θ is the surface coverage of 3-carbohydrazide on C-steel, which can be calculated by the ratio of IE/100 for different 3-carbohydrazide concentration [31]. Figs. (2-3) show the straight lines of Θ vs. C at T_1 (25°C) and T_2 (45°C), respectively.

Moreover, the adsorption heat can be calculated according to the van't Hoff equation [32]:

$$\ln K_{\text{ads}} = \Delta H^{\circ}_{\text{ads}} / RT + \text{const} \quad (4)$$

That is:

$$\ln(K_{2\text{ads}}/K_{1\text{ads}}) = -\Delta H^{\circ}_{\text{ads}}/R(1/T_2 - 1/T_1) \quad (5)$$

Where ΔH° is the adsorption heat, R is the gas constant, T is the absolute temperature, K_1 and K_2 are the adsorptive equilibrium constants at T_1 (25°C) and T_2 (45°C), respectively. In consideration that the experiments precede at the standard pressure and the solution concentrations are not very high, which are close to the standard condition, the calculated adsorption heat thus can be approximately regarded as the standard adsorption heat $\Delta H^{\circ}_{\text{ads}}$. The negative values of ΔH° Table.(4) reflect the exothermic behavior of the adsorption of 3-carbohydrazide derivatives on the C- steel surface. The standard adsorption free energy ($\Delta G^{\circ}_{\text{ads}}$) can be obtained according to the following equation [33-34].

$$K_{\text{ads}} = 1/55.5 \exp(-\Delta G^{\circ}_{\text{ads}}/RT) \quad (6)$$

The negative values of $\Delta G^{\circ}_{\text{ads}}$ (Table .4) suggest that the adsorption of 3-carbohydrazide derivatives on the C-steel surface is spontaneous. Generally, the values of $\Delta G^{\circ}_{\text{ads}}$ around or less than -20 kJ mol^{-1} are associated with the electrostatic

interaction between charged molecules and the charged metal surface (physisorption); while those around or higher than -40 kJ mol^{-1} mean charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of metal bond (chemisorption). The $\Delta G^{\circ}_{\text{ads}}$ values listed in Table (4) are around -20 kJ mol^{-1} , which means that the absorption of 3-carbohydrazide derivatives on the C-steel surface belongs to the physisorption and the adsorptive film has an electrostatic character [35-36]. Finally, the standard adsorption entropy $\Delta S^{\circ}_{\text{ads}}$ can be calculated by the following Eq:

$$\Delta S^{\circ}_{\text{ads}} = (\Delta H^{\circ}_{\text{ads}} - \Delta G^{\circ}_{\text{ads}}) / T \quad (7)$$

The ($\Delta S^{\circ}_{\text{ads}}$) values (Table 4) are positive, which are opposite to the usual expectation that the adsorption is an exothermic process and always accompanied by a decrease of entropy. The reason can be explained as follows: the adsorption of 3-carbohydrazide inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the 3-carbohydrazide compound in the aqueous phase and water molecules at the electrode surface [$\text{H}_2\text{O}_{(\text{ads})}$] [37-40]. In this situation, the adsorption of 3-carbohydrazide derivatives is accompanied by the desorption of water molecules from the electrode surface. Thus, while the adsorption process for the inhibitor is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent [41]. The thermodynamic values obtained are the algebraic sum of the adsorption of 3-carbohydrazide inhibitor molecules and the desorption of water molecules. Therefore, the gain in entropy is attributed to the increase in solvent entropy. The positive values of ($\Delta S^{\circ}_{\text{ads}}$) suggest that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of 3-carbohydrazide derivatives on the C-steel surface. Table (4) lists all the above calculated thermodynamic parameters.

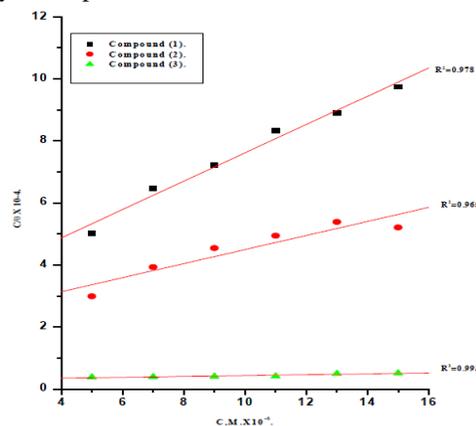


Fig. 2: Langmuir Adsorption Isotherm Plotted as (C/Θ) vs. C of 3-Carbohydrazide Derivatives for the Corrosion of C-Steel in 2 M HCl at 25°C.

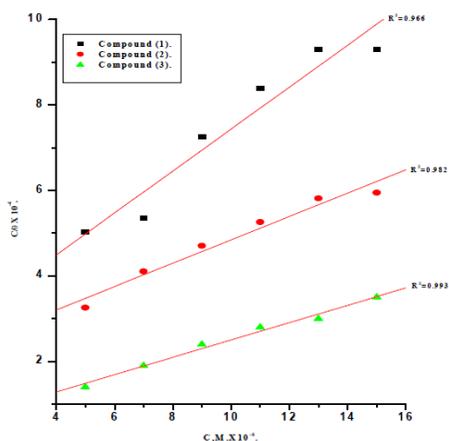


Fig. 3: Langmuir Adsorption Isotherm Plotted as (C/θ) vs. C of 3-Carbohydrazide Derivatives for the Corrosion of C-Steel in 2 M HCl at 45°C.

TABLE IV

SOME PARAMETERS FROM LANGMUIR ISOTHERM MODEL FOR C-STEEL IN 2 M HCl FOR 3-CARBOHYDRAZIDE DERIVATIVES.

Compound	Temp., K	K_{ads} M ⁻¹	$-\Delta G^{\circ}_{ads}$ kJ mol ⁻¹	$-\Delta H^{\circ}_{ads}$ kJ mol ⁻¹	ΔS°_{ads} J mol ⁻¹ K ⁻¹
1	298	0.327	7.182	5.87	4.39
	318	0.396	7.657		
2	298	0.447	7.957	5.04	9.76
	318	0.473	8.097		
3	298	0.567	8.546	1.75	22.78
	318	0.570	8.559		

A.3. Effect of Temperature

The importance of temperature variation in corrosion study involving the use of inhibitors is to determine the mode of inhibitor adsorption on the metal surface. Recently, the use of two temperatures to establish the mode of inhibitor adsorption on a metal surface has been reported and has been found to be adequate [42-43]. Thus, the influence of temperature on the corrosion behavior of C-steel in 2 M HCl in the absence and presence of 3-carbohydrazide derivatives were investigated by hydrogen evolution method at 25 and 45°C. Therefore, in examining the effect of temperature on the corrosion process, the apparent activation energies (E_a) were calculated from the Arrhenius equation [44]

$$\text{Log}(Q_2/Q_1) = (E_a/2.303R)(1/T_1 - 1/T_2) \quad (8)$$

Where Q_2 and Q_1 are the corrosion rates at temperature T_1 and T_2 respectively. An estimate of heat of adsorption was obtained from the trend of surface coverage with temperature as follows [45]:

$$Q_{ads} = 2.303R[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)] \times (T_1 \times T_2 / T_1 - T_2) \quad (9)$$

Where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2 . The calculated values for both parameters are given in Table (5). Increased activation energy (E_a) in inhibited solutions compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface while either unchanged or lower E_a in the presence of inhibitor suggest chemisorptions. It is seen from Table (5) that E_a values were higher in the presence of the additives compared to that in their absence hence leading to reduction in the corrosion rates. It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either

decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [46]. The E_a values support the earlier proposed physisorption mechanism. Hence, corrosion inhibition is assumed to occur primarily through physical adsorption on the C- steel surface, giving rise to the deactivation of these surfaces to hydrogen atom recombination. Similar results have been reported in earlier publications [47]. The negative Q_{ads} values indicate that the degree of surface coverage decreased with rise in temperature, supporting the earlier proposed physisorption mechanism [48].

TABLE V

CALCULATED VALUES OF ACTIVATION ENERGY (E_a) AND HEAT OF ADSORPTION (Q_{ads}) FOR C-STEEL IN 2 M HCl SOLUTIONS CONTAINING VARIOUS CONCENTRATIONS OF 3-CARBOHYDRAZIDE DERIVATIVES AT 25 AND 45°C OBTAINED FROM POTENTIODYNAMIC POLARIZATION MEASUREMENTS

Conc., M.	E_a kJ mol ⁻¹	$-Q_{ads}$ kJ mol ⁻¹
Blank	1.8	--
Compound (1)	5×10^{-6}	2.4
	7×10^{-6}	2.9
	9×10^{-6}	3.2
	11×10^{-6}	3.5
	13×10^{-6}	3.6
Compound (2)	15×10^{-6}	3.7
	5×10^{-6}	3.1
	7×10^{-6}	3.2
	9×10^{-6}	3.4
	11×10^{-6}	3.6
Compound (3)	13×10^{-6}	4.3
	15×10^{-6}	6.9
	5×10^{-6}	5.3
	7×10^{-6}	5.8
	9×10^{-6}	6.2
Compound (3)	11×10^{-6}	6.3
	13×10^{-6}	8.4
	15×10^{-6}	10.0
	5×10^{-6}	10.4
	7×10^{-6}	10.4

B. Electrochemical Impedance Spectroscopy (EIS)

The corrosion of C-Steel in 2 M HCl in the presence of the investigated compounds were investigated by EIS method at 25 °C after 30 min immersion. Nyquist plots in the absence and presence of investigated compound (1) is presented in Fig. (4). Similar curves were obtained for other inhibitors. It is apparent that all Nyquist plots show a single capacitive loop, both in uninhibited and inhibited solutions. The impedance data of C-steel in 2 M HCl are analyzed in terms of an equivalent circuit model Fig. (5) 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} [49] due to the charge transfer reaction. For the Nyquist plots it is obvious that low frequency data are on the right side of the plot and higher frequency data are on the left. This is true for EIS data where impedance usually falls as frequency rises (this is not true for all circuits). The capacity of double layer (C_{dl}) can be calculated from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (10)$$

Where f_{max} is maximum frequency. The parameters obtained from impedance measurements are given in Table (6). It can be seen from Table (6) that the values of charge transfer resistance R_{ct} increase with inhibitor concentration [50]. In the case of

impedance studies, % IE increases with inhibitor concentration in the presence of investigated inhibitors and the % IE of these investigated inhibitors is as follows:

Compound (3) > Compound (2) > Compound (1)

The impedance study confirms the inhibiting characters of these compounds obtained from potentiodynamic polarization. It is also noted that the (C_{dl}) values tend to decrease when the concentration of these compounds increases. This decrease in (C_{dl}), which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that these compounds molecules function by adsorption at the metal/solution interface^[51]. The inhibiting effect of these compounds can be attributed to their parallel adsorption at the metal solution interface. The parallel adsorption is owing to the presence of one or more active center for adsorption.

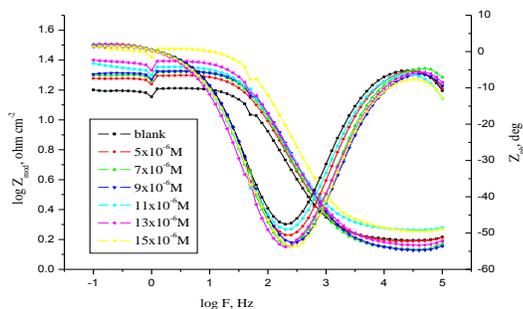
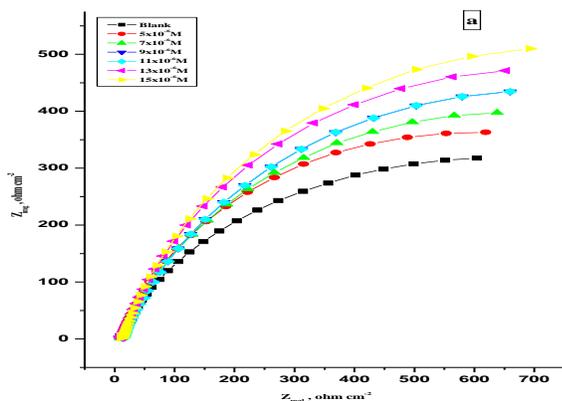


Fig. 4. The Nyquist (a) and Bode (b) Plots for Corrosion of C-Steel in 2 M HCl in the Absence and Presence of Different Concentrations of Compound (1) at 25°C.

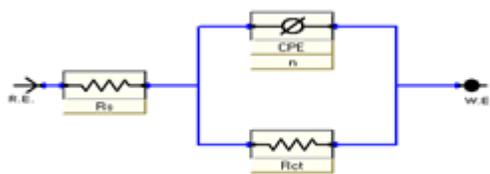


Fig. 5. Equivalent Circuit Model used to Fit the Impedance Spectra

TABLE VI
ELECTROCHEMICAL KINETIC PARAMETERS OBTAINED FROM EIS TECHNIQUE FOR THE CORROSION OF C-STEEL IN 2 M HCL AT DIFFERENT CONCENTRATIONS OF INVESTIGATED INHIBITORS AT 25 °C.

Cpd	Conc., M	R_s , Ωcm^2	$Y_0 \times 10^{-3}$, $\mu\Omega^{-1}\text{s}^n$	n	R_{ct} , Ωcm^2	$C_{dl} \times 10^{-2}$, μFcm^{-2}	θ	%IE
(1)	Blank	13.30	169.9	746.7	1.047	80.79	-----	-----
	5×10^{-6}	13.28	169.5	743.8	1.256	80.19	0.1664	16.64
	7×10^{-6}	13.29	169.4	743.6	1.258	80.06	0.1677	16.77
	9×10^{-6}	10.92	157.1	777.2	1.328	75.82	0.2115	21.15
	11×10^{-6}	10.65	171.5	769.8	1.330	75.22	0.2127	21.27
	13×10^{-6}	10.65	171.4	769.6	1.331	75.66	0.2133	21.33
(2)	15×10^{-6}	10.92	123.1	742.7	1.367	73.65	0.2340	23.40
	5×10^{-6}	10.39	122.9	742.9	1.369	73.60	0.2346	23.46
	7×10^{-6}	5.992	157.6	769.4	1.375	73.23	0.2385	23.85
	9×10^{-6}	9.183	136.3	760.0	1.465	68.73	0.2853	28.52
	11×10^{-6}	9.175	136.5	759.9	1.466	68.69	0.2858	28.58
	13×10^{-6}	10.11	126.7	764.2	1.476	68.21	0.2906	29.06
(3)	15×10^{-6}	10.10	126.7	764.2	1.477	68.16	0.2911	29.11
	5×10^{-6}	10.51	166.8	758.3	1.542	65.32	0.3210	32.10
	7×10^{-6}	11.35	157.3	769.7	1.556	64.72	0.3271	32.71
	9×10^{-6}	11.35	157.4	769.6	1.558	64.64	0.3279	32.97
	11×10^{-6}	9.876	163.7	767.1	1.736	58.02	0.3968	39.68
	13×10^{-6}	15.16	152.9	772.0	1.879	53.61	0.4427	44.27
	15×10^{-6}	15.17	153.0	773.0	1.880	53.58	0.4430	44.30

C. Electrochemical Frequency Modulation Technique (EFM)

EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current value without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring^[52]. The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. Figs (6) shows the frequency spectrum of the current response of C-steel in 2 M HCl, contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies. The EFM intermodulation spectrums of C-steel in 2 M HCl acid solution containing (5×10^{-6} - 15×10^{-6} M) of the studied inhibitors are shown in Fig (6). Similar results were recorded for the other concentrations of the investigated compound (not shown). The harmonic and intermodulation peaks are clearly visible and are much larger than the background noise. The two large peaks, with amplitude of about 200 μA , are the response to the 40 and 100 mHz (2 and 5 Hz) excitation frequencies. It is important to note that between the peaks there is nearly no current response (<100 nA). The experimental EFM data were treated using two

different models: complete diffusion control of the cathodic reaction and the “activation” model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode [53]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors (CF-2 and CF-3). These electrochemical parameters were simultaneously determined by Gamry EFM140 software, and listed in Table (7). The data presented in Table (7) obviously show that, the addition of any one of tested compounds at a given concentration to the acidic solution decreases the corrosion current density, indicating that these compounds inhibit the corrosion of C-steel in 2 M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality [54]. The inhibition efficiencies $\text{IE}_{\text{EFM}} \%$ increase by increasing the studied inhibitor concentrations and was calculated as follows:

$$\% \text{IE}_{\text{EFM}} = \left[1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \right] \quad (11)$$

Where i_{corr}^0 and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively. The inhibition sufficiency obtained from this method is in the order: Compound(3) > Compound(2) > Compound(1).

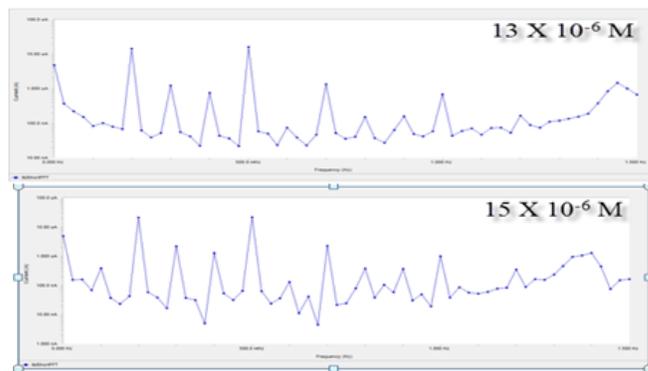
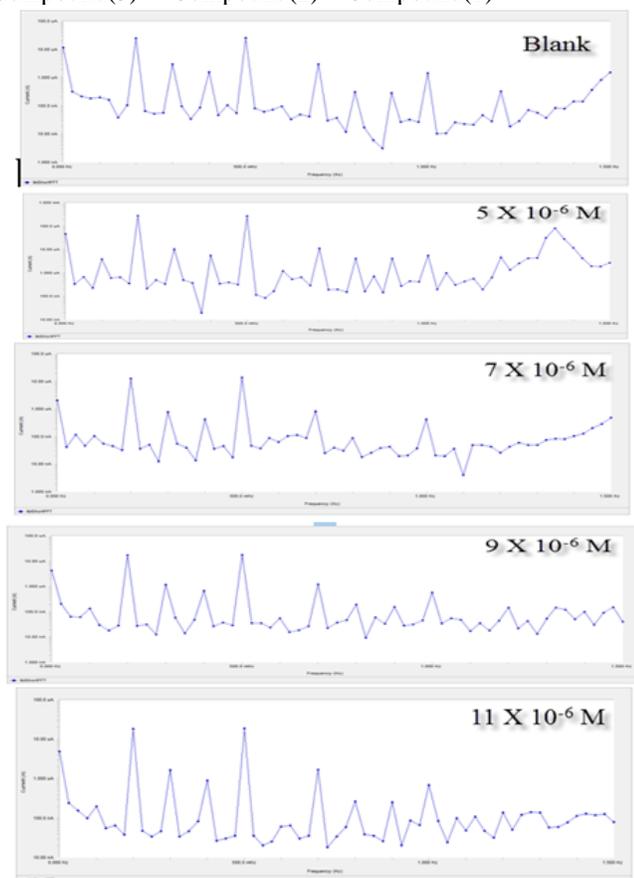


Fig. 6. EFM Spectra C-Steel in 2 M HCl in the Absence and Presence of Different Concentrations of Compound (1) at 25°C.

TABLE VII

ELECTROCHEMICAL KINETIC PARAMETERS OBTAINED FROM EFM TECHNIQUE FOR THE CORROSION OF C-STEEL IN 2 M HCL AT DIFFERENT CONCENTRATIONS OF INVESTIGATED INHIBITORS AT 25 °C.

Cpd	Conc., M.	i_{corr} , μAcm^{-2}	B_c , mV dec^{-1}	B_a , mV dec^{-1}	CF-2	CF-3	CR mpv	θ	%IE
	Blank	52.24	96.49	327.3	1.97	3.45	26.16	-	-
(1)	5×10^{-6}	40.10	85.35	107.9	1.93	2.92	22.30	0.23	23.2
	7×10^{-6}	38.66	140.9	297.5	1.89	2.38	17.71	0.25	25.9
	9×10^{-6}	36.68	105.6	190.0	1.93	3.27	16.76	0.29	29.4
	11×10^{-6}	35.36	92.57	188.8	2.07	3.06	16.16	0.32	32.3
	13×10^{-6}	33.62	104.4	225.7	1.77	3.74	15.36	0.35	35.6
(2)	5×10^{-6}	32.86	75.56	147.2	1.95	2.50	15.02	0.37	37.9
	7×10^{-6}	32.44	90.23	191.2	2.02	2.95	14.83	0.37	73.1
	9×10^{-6}	31.77	140.9	297.5	1.89	2.89	13.47	0.39	39.1
	11×10^{-6}	29.10	78.8	89.8	2.41	2.89	13.33	0.44	44.2
	13×10^{-6}	27.71	90.74	194.9	1.93	2.41	12.66	0.46	46.9
(3)	5×10^{-6}	26.73	83.8	160.3	1.82	3.60	12.21	0.48	48.8
	7×10^{-6}	26.65	91.51	164.5	1.92	2.76	12.31	0.48	48.9
	9×10^{-6}	22.05	87.25	351.9	1.92	3.18	10.50	0.57	57.7
	11×10^{-6}	19.22	83.04	128.7	1.87	2.81	8.78	0.63	63.2
	13×10^{-6}	17.23	87.22	146.2	1.83	2.95	6.95	0.67	67.0
	11×10^{-6}	17.20	45.7	48.4	1.89	3.19	5.36	0.67	67.1
	13×10^{-6}	16.89	73.36	105.3	1.85	3.17	6.80	0.67	67.6
	15×10^{-6}	15.53	53.38	67.57	2.17	2.62	4.35	0.70	70.2

D. Quantum Chemical Calculations

Theoretical calculations were performed for only the neutral forms, in order to give further insight into the experimental results. Values of quantum chemical indices such as energies of LUMO and HOMO (E_{HOMO} and E_{LUMO}), the formation heat ΔH_f and energy gap ΔE , are calculated by semi-empirical AM1, MNDO and PM3 methods has been given in Table (8). The reactive ability of the inhibitor is related to E_{HOMO} , E_{LUMO} [55]. Higher E_{HOMO} of the adsorbent leads to higher electron donating ability [56]. Low E_{LUMO} indicates that the acceptor accepts electrons easily. The calculated quantum chemical indices (E_{HOMO} , E_{LUMO} , μ) of investigated compounds are shown in Table (8). The difference $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ is the energy required to move an electron from HOMO to LUMO. Low ΔE facilitates adsorption of the molecule and thus will cause higher inhibition efficiency.

The bond gap energy ΔE increases from (3 to 1). This fact explains the decreasing inhibition efficiency in this order (3 > 2 > 1), as shown in Table (8) and Fig. (7) show the optimized structures of the three investigated compounds. So, the calculated energy gaps show reasonably good correlation with the efficiency of corrosion inhibition. Table (8) also indicates that compound (3) possesses the lowest total energy that means that compound (3) adsorption occurs easily and is favored by the highest softness. The HOMO and LUMO electronic density distributions of these molecules were plotted in Fig. (7). For the HOMO of the studied compounds that the

benzene ring, N-atoms and O-atom have a large electron density. The data presented in Table. (8) show that the calculated dipole moment decrease from (3> 2>1).

TABLE VIII
THE CALCULATED QUANTUM CHEMICAL PROPERTIES FOR ORGANIC COMPOUNDS.

	Cpd (1)	Cpd (2)	Cpd (3)
-E _{HOMO} (eV)	8.538	8.501	8.248
-E _{LUMO} (eV)	0.192	0.868	0.898
ΔE (eV)	8.346	7.633	7.350
η (eV)	4.173	3.817	3.675
σ (eV ⁻¹)	0.240	0.262	0.272
-Pi (eV)	4.365	4.685	4.573
χ (eV)	4.365	4.685	4.573
Dipole Moment (Debye)	3.424	3.794	5.670

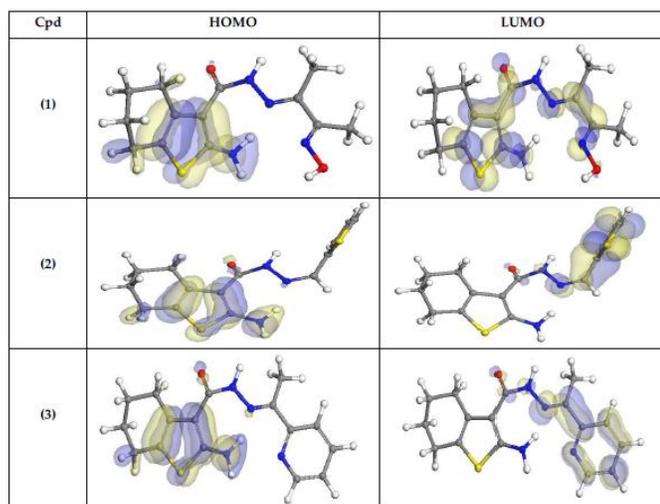


Fig. 7. Molecular Orbital Plots of Organic Compounds

E. Chemical Structure of the Inhibitors and Corrosion Inhibition

Inhibition of the corrosion of C-steel in 2 M HCl solution by some 3-carbohydrazone derivatives is determined by potentiodynamic anodic polarization measurements and other methods, it was found that the inhibition efficiency depends on concentration, nature of metal, the mode of adsorption of the inhibitors and surface conditions. The observed corrosion data in presence of these inhibitors, namely:

- i) The decrease of corrosion rate and corrosion current with increase in concentration of the inhibitor
- ii) The linear variation of weight loss with time
- iii) The shift in Tafel lines to higher and lower potential regions
- iv) The decrease in corrosion inhibition with increasing temperature indicates that desorption of the adsorbed inhibitor molecules takes place and
- v) The inhibition efficiency was shown to depend on the number of adsorption active centers in the molecule and their charge density.

The corrosion inhibition is due to adsorption of the inhibitors at the electrode/ solution interface, the extent of adsorption of an inhibitor depends on the nature of the metal, the mode of adsorption of the inhibitor and the surface conditions. Adsorption on C-steel surface is assumed to take place mainly

through the active centers attached to the inhibitor and would depend on their charge density. Transfer of lone pairs of electrons on the nitrogen atoms to the C- steel surface to form a coordinate type of linkage is favored by the presence of a vacant orbital in iron atom of low energy. Polar character of substituents in the changing part of the inhibitor molecule seems to have a prominent effect on the electron charge density of the molecule. It was concluded that the mode of adsorption depends on the affinity of the metal towards the π -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 was as follow: Compound (3) > Compound (2) > Compound (1) .

Compound (3) exhibits excellent inhibition power due to: (i) its larger molecular size (341.41) that may facilitate better surface coverage, and (ii) the presence electron releasing groups (4N, 1O and 1S atoms) which enhance the delocalized π -electrons on the active centers of the compound. Compound (2) comes after compound (1) in inhibition efficiency because it has lesser molecular size (305.42) and 1O, 2S and 3N atoms as active centers. Compound (3) has the lowest inhibition efficiency, this is due to it has the lowest molecular size (294.37)

IV. CONCLUSIONS

- 1) The tested 3-carbohydrazone derivatives establish a very good inhibition for C- steel corrosion in HCl solution.
- 2) 3-carbohydrazone derivatives inhibit C-steel corrosion by adsorption on its surface and act better than the passive oxide film.
- 3) The inhibition efficiency is in accordance to the order: (3) > (2) > (1).
- 4) The inhibition efficiencies of the tested compounds increase with increasing of their concentrations.
- 5) Double layer capacitances decrease with respect to blank solution when the inhibitor added. This fact may explained by adsorption of the inhibitor molecule on the C-steel surface.
- 6) The adsorption of these compounds on carbon steel surface in HCl solution follows Langmuir adsorption isotherm.
- 7) The values of inhibition efficiencies obtained from the different independent techniques showed the validity of the obtained results.

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