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New Benzonitrile Azo Dyes as Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid Solutions

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Inhibition of carbon steel corrosion by some benzonitrile azo dyes in 1 M HCl has been studied using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. The electrochemical measurements showed that the inhibition efficiency increased by increasing the inhibitor concentration. The potentiodynamic polarization measurements indicated that the inhibitors are of mixed type. The results of EIS indicate that the corrosion resistance of the adsorption film formed by inhibitor on metal surface has increased. EFM can be used as a rapid and non-destructive technique for corrosion rate measurements without prior knowledge of Tafel constants. The results obtained from the three different techniques were in good agreement.

Keywords: Carbon steel, HCl, benzonitrile derivatives, potentiodynamic polarization, EIS, EFM

1. INTRODUCTION

Carbon steel, the most widely used engineering material, accounts for approximately 85% of the annual steel production worldwide. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal-processing equipment. Azo dye derivatives have attracted considerable attention due to their versatile application in various fields, including textile, leather, cosmetic, pharmaceutical, food, and in high technology areas like laser, liquid crystalline displays, electro optical devices and ink-jet printers [1, 2] The use of inhibitors is one of the most practical methods for protection against corrosion. The concentration of a given inhibitor needed to protect a metal will depends on number of factors: such as (i) composition of the environment, (ii) temperature, (iii) velocity of the liquid, (iv) the presence or absence in the metal of internal or external stresses, (v) composition of the metal, and the presence of any other metal content. Several works have studied the influence of organic compounds containing nitrogen on the corrosion of steel in acidic media [3–14]. These inhibitors are adsorbed on the metal surface and protect the metal surface from the corrosive medium. Adsorption of these compounds on metal surface depends on: (i) nature and charge of the metal, (ii) the type of electrolyte, and (iii) the chemical structure of the inhibitor. The inhibition efficiency was found to depend on some physic-chemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons [15, 16].

The present work was designed to study the corrosion inhibition of carbon steel in 1 M HCl solutions by some new benzonitrile azo dyes as corrosion inhibitors using three different techniques: potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM).

2. EXPERIMENTAL

2.1. Inhibitors

The inhibitors were synthesized in the laboratory [17] and characterized by spectral analysis methods. Its structures were established by spectral measurements. The structure formula of the investigated compounds is given in Table 1. All chemicals used are of analytical grades.

2.2. Corrosion medium

1 M HCl solution was prepared by dilution with double distilled water, the concentartion ranges of investigated compounds were ($1x10^{-6}$-$13x10^{-6}$) and were prepared from ethanol.

2.3. Electrochemical measurements

Three different electrochemical techniques have been employed for studying the inhibition of *C*-steel corrosion by benzonitrile compounds, these are: Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) methods.

Electrochemical experiments were performed in a conventional three-electrode electrochemical cell at 25°C, consisting of carbon steel electrode with an exposed area of 1 cm^2 as working electrode, a saturated calomel electrode as reference electrode, and a platinum sheet (1 cm^2) as counter electrode were used for electrochemical studies

2.3.1. Potentiodynamic polarization Technique

The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -1500 mV to +500 mV with scanning rate of 1 mVs^{-1} using Gamry framework instruments (version 3.20). Corrosion current densities (j_{corr}) and corrosion potential (E_{corr}), were evaluated from intersection of the linear anodic and cathodic branches of Tafel plots and all of them will calculated in the absence and presence of different concentrations of inhibitors. The degree of surface coverage (θ) and the percentage inhibition efficiency (% IE) were calculated using equation (1):

$$\% \text{ IE} = \theta \text{ x } 100 = [1 - (i_{corr} / i^{o}_{corr})] \text{ x } 100 \quad (1)$$

where i^{o}_{corr} and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively.

2.3.2. Electrochemical impedance spectroscopy (EIS) Technique

The EIS spectra were recorded at open circuit potential, OCP after immersion the electrode for 15 minutes. The AC signal was 5 mV peak to peak and the frequency range studied was between 0.1-10^5 Hz. The data were presented as Nyquist and Bode plots. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer (R_{ct}) and the capacity of double layer which is calculated from equation (2):

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

where f is the maximum frequency, R_{ct} is the resistance of charge transfer.

The degree of surface coverage (θ) and the percentage inhibition efficiency (% IE) were calculated using equation (3):

$$\%\text{IE} + \theta \text{ x } 100 = [1 - (R^{\circ}_{ct} / R_{ct})] \quad (3)$$

where R°_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of different concentrations of inhibitor, respectively.

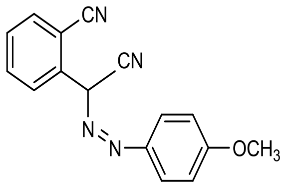
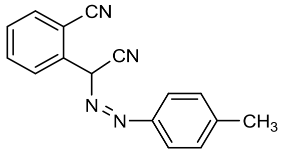
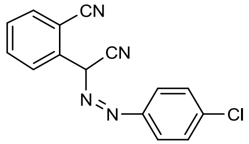
2.3.3. Electrochemical frequency modulation technique (EFM)

Electrochemical frequency modulation technique, EFM, was carried out using two frequencies 2 Hz and 5 Hz. The base frequency was 1 Hz, so the waveform repeats after 1 second. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. The electrode potential was allowed to stabilize 30 min before starting the measurements.

The percentage of inhibition efficiency (% IE) is calculated as given in Eq. (1).

All electrochemical experiments were carried out using Gamry PCI 300/4 Potentiostat/ Galvanostat/ Zra analyzer, DC 105 corrosion software, EIS 300 Electrochemical impedance software, EFM 140 Electrochemical frequency modulation software and Echem Analyst 5.21 for results plotting, graphing, data fitting and calculating.

Table 1. Characterization data of the benzonitrile inhibitors

Inhibitor	**St**	**Structure**	**Name**	**Mol. Wt., Chem. formula**
1			(Z)-2-(cyano((4-methoxyphenyl) diazenyl)methyl)benzonitrile	276.29 $C_{16}H_{12}N_4O$
2			(Z)-2-(cyano(p-tolyldiazenyl)methyl)benzonitrile	260.29 $C_{16}H_{12}N_4$
3			(Z)-2-(((4-chlorophenyl)diazenyl)(cyano)methyl) benzonitrile	280.5 $C_{15}H_9ClN_4$

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic Polarization

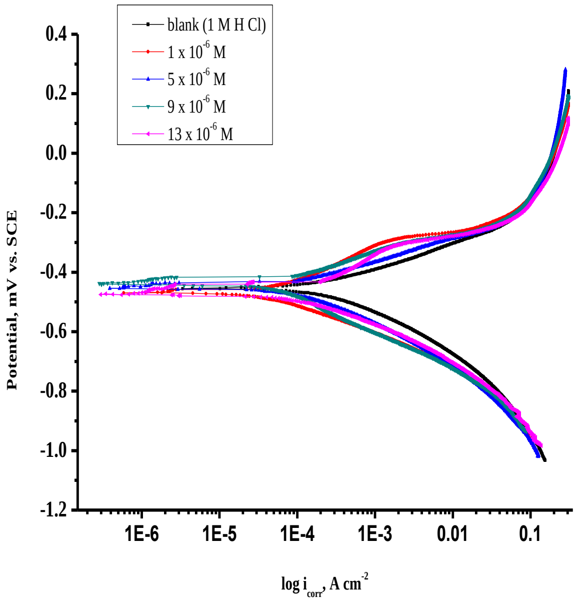


Figure 1. Potentiodynamic polarization curves for the dissolution of carbon steel in 1 M HCl in the absence and presence of different concentrations of compound (1) at 25°C

Potentiodynamic polarization curves of carbon steel in 1 M Hl solutions in the absence and presence of different concentrations of compound (1) at 25 °C are shown in Fig. 1. Similar curves were obtained for other compounds (not shown).

The numerical values of the variation of corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel slopes (b_a and b_c), degree of surface coverage (θ) and inhibition efficiency (% IE) with the concentrations of the investigated compounds are given in Table 2.

Table 2. Corrosion parameters obtained from potentiodynamic polarization of carbon steel in 1 M HCl containing various concentrations of the investigated compounds at 25 °C

Compound	**Conc. M**	**-E_{corr} mV vs. SCE**	**i_{corr} µA cm^{-2}**	**b_a mV dec^{-1}**	**b_c mV dec^{-1}**	**θ**	**% IE**	**CR mm yr^{-1}**	**R_p Ω cm^2**
Blank	1M HCl	455	636.9	233	223	----	----	7.394	77.75
1	1x10^{-6}	469	50.2	164	139	0.921	92.1	0.583	652.3
	5x10^{-6}	451	9.4	154	128	0.985	98.5	0.109	3242
	9x10^{-6}	439	5.7	131	111	0.991	99.1	0.067	4557
	13x10^{-6}	475	3.4	117	104	0.995	99.5	0.039	7139
2	1x10^{-6}	458	81.7	175	152	0.872	87.2	0.949	433
	5x10^{-6}	510	60.7	175	136	0.905	90.5	0.704	546.7
	9x10^{-6}	432	26.4	159	135	0.959	95.9	0.307	1204
	13x10^{-6}	467	13.5	127	120	0.979	97.9	0.156	1992
3	1x10^{-6}	469	187.8	187	167	0.705	70.5	2.180	204.4
	5x10^{-6}	468	72.6	172	147	0.886	88.6	0.843	474.3
	9x10^{-6}	460	64.8	138	143	0.898	89.8	0.752	470.6
	13x10^{-6}	466	23.9	129	126	0.962	96.2	0.278	1158

It was found that the increase in inhibitor concentration has resulted in the following:

1- Increase of both cathodic and anodic overvoltages and caused parallel displacement to the more negative and positive values, respectively. This indicates that there is no change in the mechanism of the process.

2- The corrosion current density (i_{corr}) decreases with increasing the concentration of benzonitrile derivatives. Which indicates that the presence of these compounds inhibit the dissolution of carbon steel in 1 M HCl solution and the degree of inhibition depends on the concentration and type of inhibitors used.

3- The presence of these compounds resulted in a slightly shift of corrosion potential towards the active direction in comparison to the result obtained in the absence of the inhibitor. The investigated compounds appeared to act as mixed type inhibitors.

4- Increase of both anodic and cathodic Tafel slopes indicates a mixed anodic and cathodic effect on the corrosion mechanism [18] i.e. mixed inhibitor. The higher values of Tafel slope can be attributed to surface kinetic process rather the diffusion-controlled process [19].

5- It is found that, R_p increases with increasing of benzonitrile derivatives concentration.

6- The order of decreasing inhibition efficiency of the investigated compounds is as follows: 1 > 2 > 3

3.2. Electrochemical Impedance Spectroscopy (EIS)

The corrosion of carbon steel in 1 M HCl solution in the absence and presence of different concentrations of benzonitrile derivatives was investigated by the EIS technique at 25 °C.

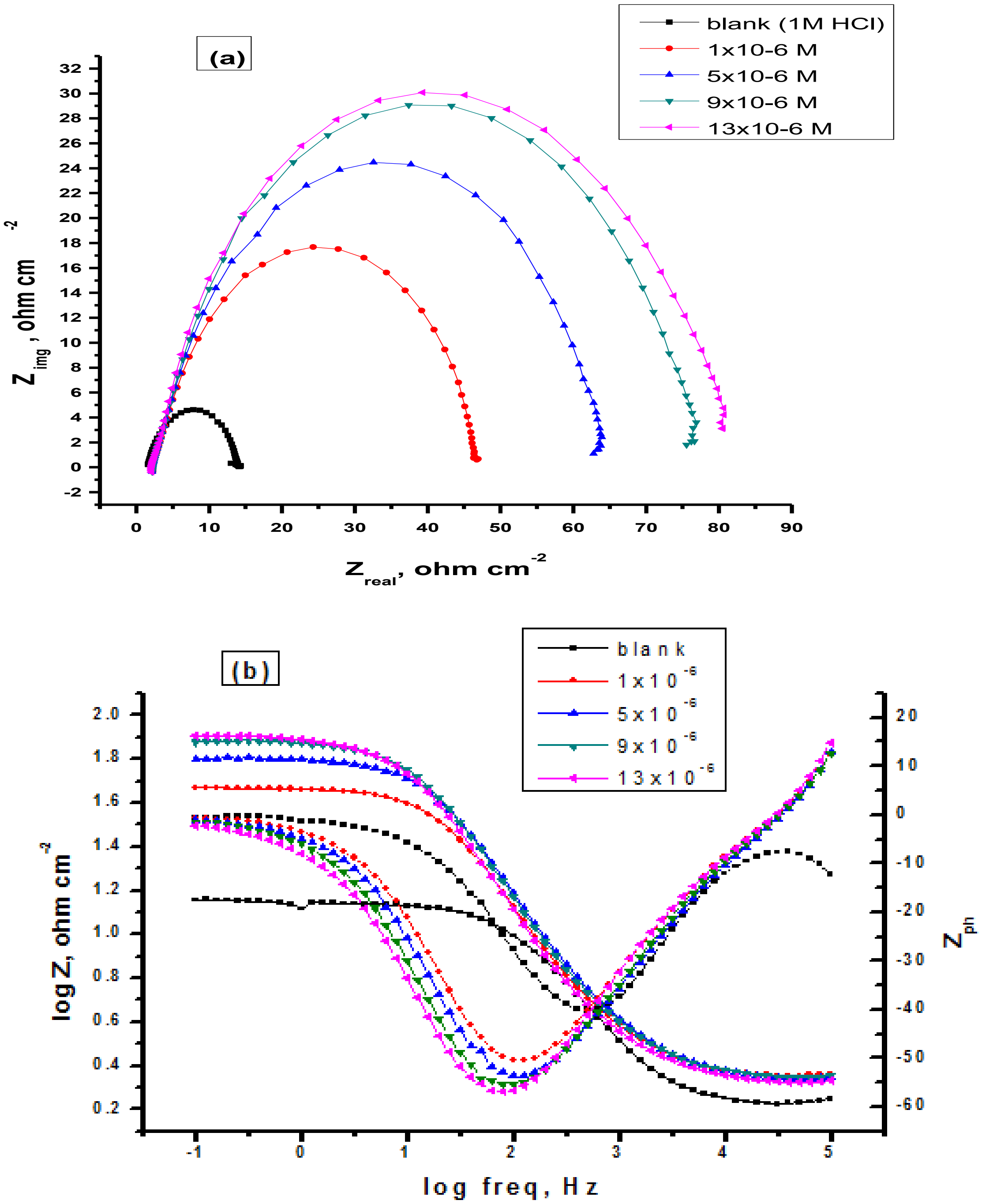


Figure 2. The Nyquist (a) and Bode **(b)** plots for corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of compound (1) at 25 °C

Nyquist plots (a) and bode plots (b) for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of investigated compound (1) are shown in Figure (2). Similar curves were obtained for other inhibitors (not shown). The obtained Nyquist impedance diagrams in most cases does not show perfect semicircle, generally attributed to the frequency dispersion [20] as a result of roughness and inhomogenities of the electrode surface. The data reveals that, each impedance diagram consists of a large capacitive loop with low frequencies dispersion (inductive arc). This inductive arc is generally attributed to anodic adsorbed intermediates controlling the anodic processes [21, 22]. By following this, inductive arc was disregarded. The Nyquist impedance diagrams show single capacitive loop, which is attributed to charge transfer of the corrosion process, and the diameters of the loops increase with increasing the concentration of inhibitors.

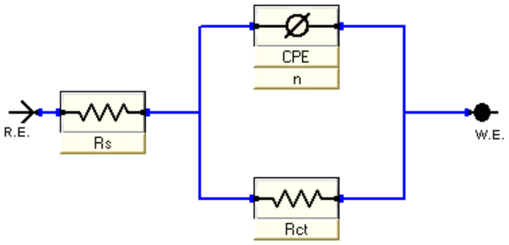


Figure 3. The equivalent circuit model used to fit the experimental results

The impedance spectra of the different Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit model as given in Figure (3), 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} [23]. The capacity of double layer C_{dl} is calculated from equation (2). The surface coverage (θ) and the inhibition efficiency obtained from impedance measurements are calculated from the equation (3)

Table 3. Electrochemical kinetic parameters obtained from EIS technique for the corrosion of carbon steel in 1 M HCl at different concentrations of the investigated compounds at 25 °C

Compound	**Conc. M**	**C_{dl} µF cm^{-2}**	**R_{ct} Ω cm^2**	**θ**	**% IE**
Blank	1M HCl	34.7	12.4	----	----
1	$1x10^{-6}$	26.3	45.4	0.726	72.6
	$5x10^{-6}$	25.9	63.3	0.804	80.4
	$9x10^{-6}$	25.4	76.3	0.837	83.7
	$13x10^{-6}$	24.9	80.1	0.845	84.5
2	$1x10^{-6}$	30.4	27.99	0.556	55.6
	$5x10^{-6}$	28.7	33.06	0.624	62.4
	$9x10^{-6}$	26.8	37.57	0.669	66.9
	$13x10^{-6}$	25.3	47.51	0.738	73.8
3	$1x10^{-6}$	29.1	22.25	0.441	44.1
	$5x10^{-6}$	28.2	30.72	0.595	59.5
	$9x10^{-6}$	27.8	34.59	0.641	64.1
	$13x10^{-6}$	26.1	43.83	0.716	71.6

From the impedance data given in Table 3, it was found that:

The value of R_{ct} increases with increasing the concentration of the inhibitor and hence, the increase in the corrosion inhibition efficiency in acidic medium. This can be attributed to the formation of protective film on the metal solution interface [24].

The inhibition efficiency has increased with increase in inhibitor concentration, which may have resulted due to the contact adsorption film. The C_{dl} value tends to decrease due to the displacement of the water molecules by the inhibitor molecules at the interface of the electrical double layer, which suggested that the inhibitors molecules function by adsorption at the metal solution interface [25], and the charge transfer between the solution and metal surface has been inhibited sharply.

It was found that R_{ct} has increased with increasing inhibitor concentration, which confirms the increase in corrosion resistance of the adsorption film formed by the inhibitor on the metal surface, therefore, the corrosion rate has decreased. The order of inhibition efficiency obtained from EIS measurements is: 1 > 2 > 3

3.3. The Electrochemical Frequency Modulation Technique (EFM)

Electrochemical frequency modulation is a non-destructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Like EIS, it is a small signal ac technique.

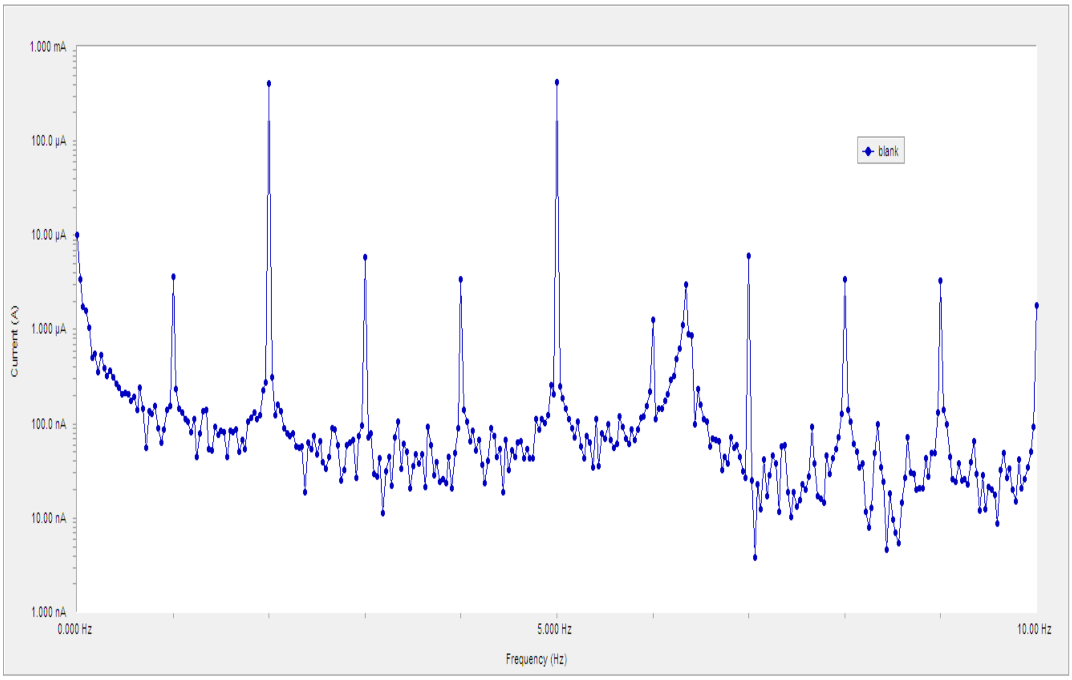


Figure 4. Intermodulation spectrum for carbon steel in 1 M HCl of blank at 25 °C

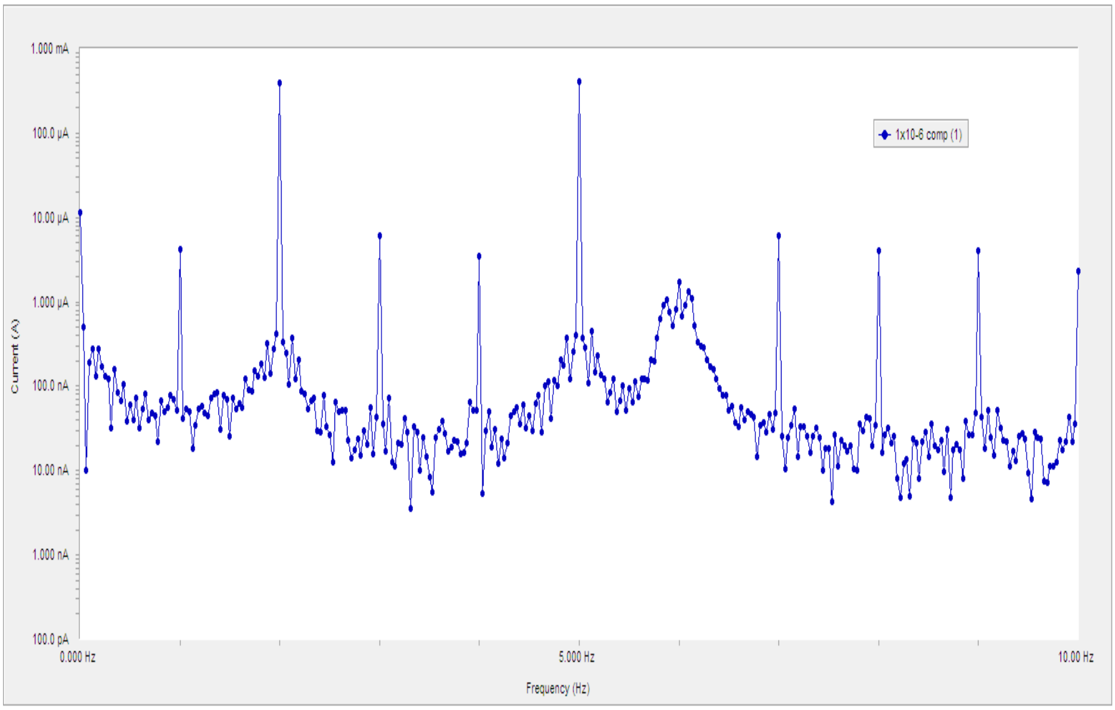


Figure 5. Intermodulation spectrum for carbon steel in 1 M HCl in presence of 1x10^{-6} M inhibitor (1) at 25 $^{\circ}$C

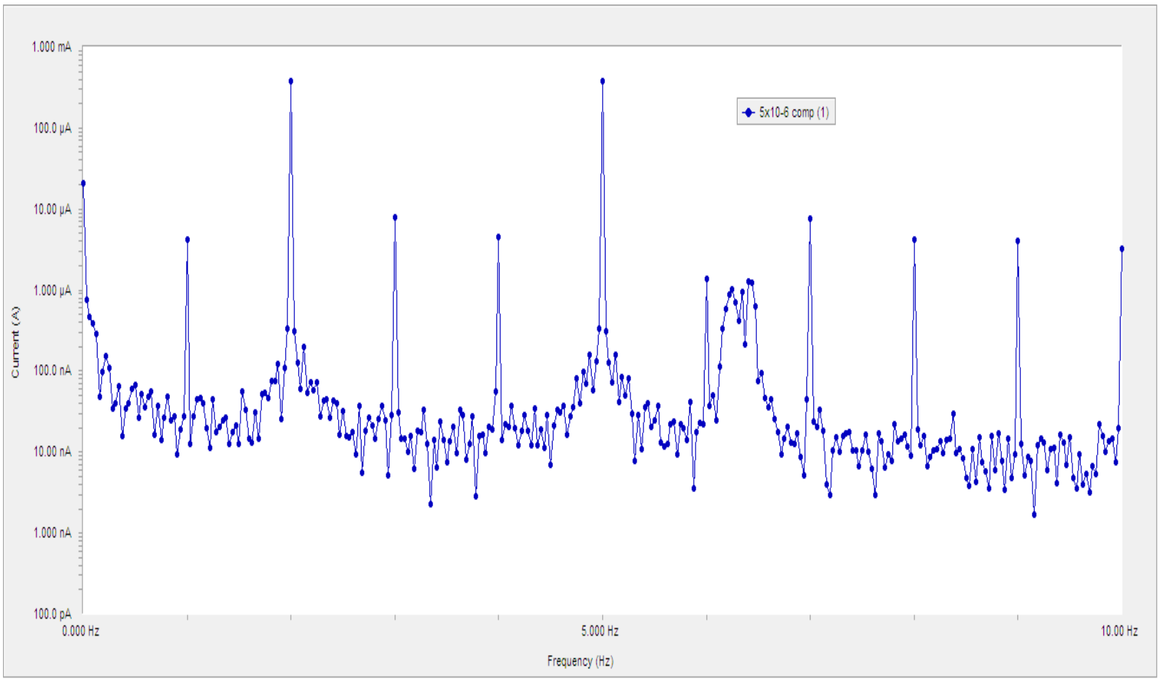


Figure 6. Intermodulation spectrum for carbon steel in 1 M HCl in presence of 5x10^{-6} M of inhibitor (1) at 25 $^{\circ}$C

Figures (4-8) represents the EFM intermodulation spectra of carbon steel in 1 M HCl in the absence and presence of different concentrations of compound (1) at 25 $^{\circ}$C. Similar intermodulation spectra were obtained for other compounds (not shown). Each spectrum is a current response as a function of frequency. The two large peaks, with amplitudes of about 200 microampere, are the response to the 2 Hz and 5 Hz while the peaks with lower amplitudes (between 1 and 20 microampere) are the harmonics. These larger peaks were used by the Gamry EFM140 software to calculate the corrosion current density (i_{corr}), Tafel constants (b_a and b_c) and causality factors, CF-2, CF-3.

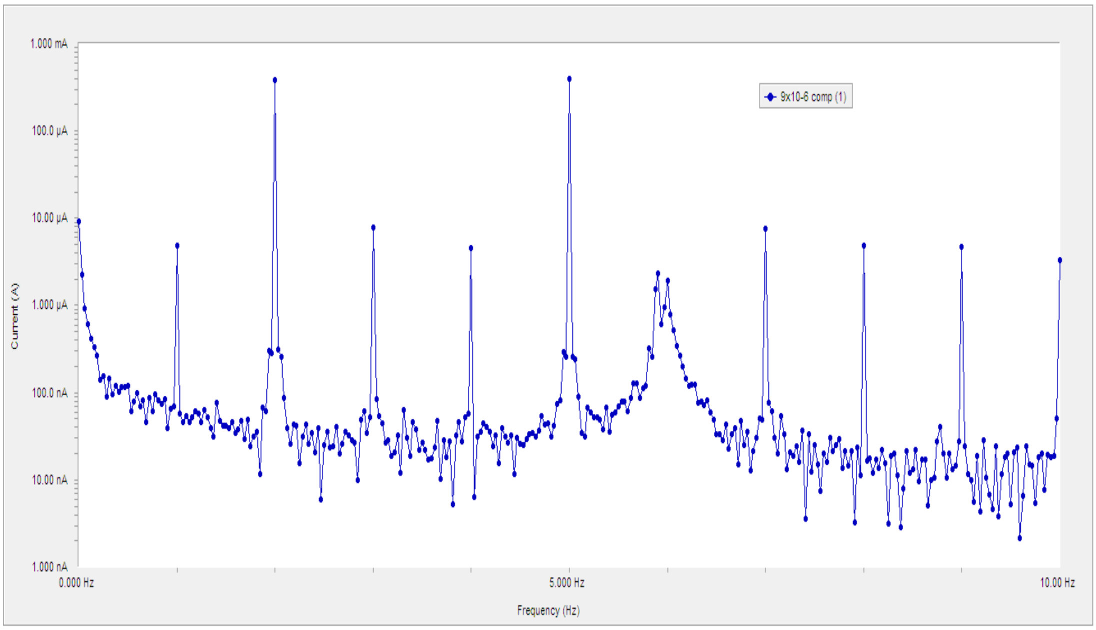


Figure 7. Intermodulation spectrum for carbon steel in 1 M HCl in presence of 9 x 10^{-6} M of inhibitor (1) at 25 °C

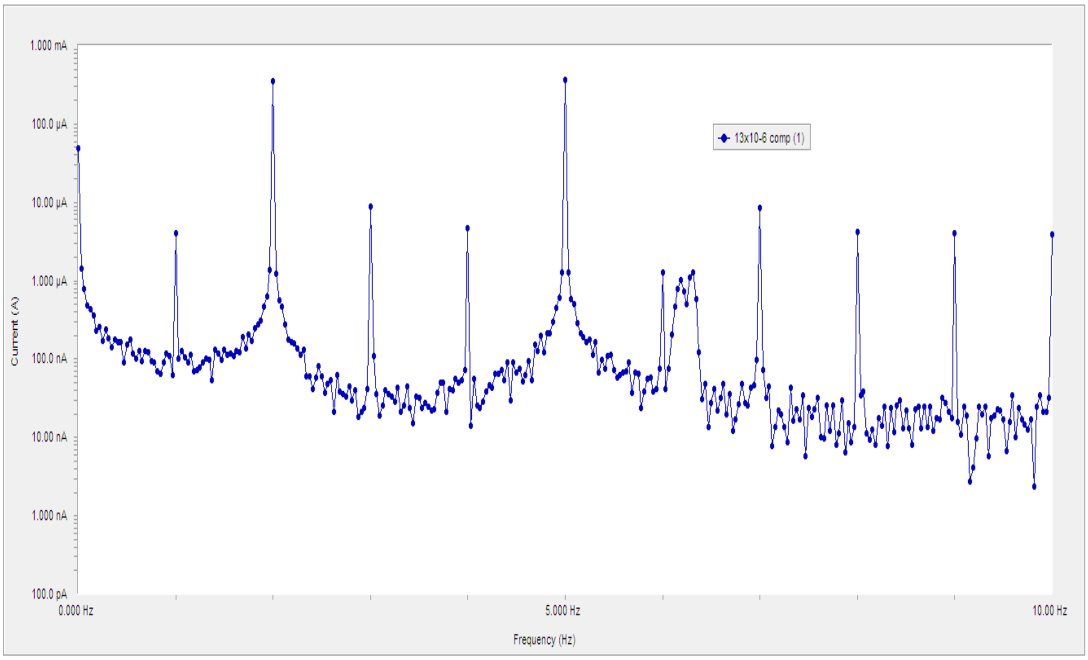


Figure 8. Intermodulation spectrum for carbon steel in 1 M HCl in presence of $13x10^{-6}$ M of inhibitor (1) at 25 °C

The corrosion parameters such as inhibition efficiency (% IE), corrosion current density (i_{corr}), Tafel constants (b_a and b_c) and causality factors, CF-2, CF-3, at different concentrations of benzonitrile derivatives compounds in 1 M HCl at 25 °C are presented in Table (4).

Table 4. Electrochemical kinetic parameters obtained from EFM for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of the investigated compounds at 25 °C

Compound	**Conc. M**	**i_{corr} μA cm^{-2}**	**b_a mV dec^{-1}**	**b_c mV dec^{-1}**	**CF-2**	**CF-3**	**CR mpy**	**θ**	**% IE**
Blank	1M HCl	813.9	121	135	2.293	3.121	363.0	----	----
3	$1x10^{-6}$	717.5	109	122	2.100	3.227	320.0	0.118	11.8
	$5x10^{-6}$	650.7	104	119	1.975	3.136	290.2	0.201	20.1
	$9x10^{-6}$	623.0	98	112	1.985	2.818	277.8	0.235	23.5
	$13x10^{-6}$	592.0	100	118	2.017	3.204	264.0	0.273	27.3
2	$1x10^{-6}$	553.5	102	118	1.985	3.296	246.9	0.319	31.9
	$5x10^{-6}$	535.3	101	114	2.029	3.194	238.7	0.342	34.2
	$9x10^{-6}$	521.1	98	112	2.010	2.880	232.4	0.359	35.9
	$13x10^{-6}$	500.3	106	113	1.932	3.046	223.1	0.385	38.5
1	$1x10^{-6}$	442.4	99	111	1.977	2.869	197.3	0.456	45.6
	$5x10^{-6}$	396.4	99	111	2.011	3.452	176.8	0.513	51.3
	$9x10^{-6}$	347.2	101	120	2.052	3.406	154.8	0.573	57.3
	$13x10^{-6}$	339.6	99	110	2.046	3.113	151.4	0.583	58.3

It is observed from the table that the corrosion current densities decreased by increasing the concentrations of the different inhibitors.

The standard values for CF-2 and CF-3 are 2 and 3, respectively. The causality factor is calculated from the frequency spectrum of the current response. The values of causality factors obtained under different experimental conditions are approximately equal the theoretical values (2 and 3) indicating that the measured data are of good quality [26]. The values of corrosion current density (i_{corr}) decreased by increasing the different concentrations of the investigated compounds at 25 °C, indicating that the compounds inhibit the corrosion of carbon steel in HCl solution through adsorption on carbon steel surface. The values of b_a and b_c decreases with increasing the concentrations of the investigated compounds at 25 °C. The inhibition efficiency increased with increasing the inhibitor concentrations, the inhibition efficiency (% IE) is calculated from equation (1).

It is clear that the data obtained from chemical and electrochemical measurements were in a good agreement with the results obtained from EFM. The order of decreasing the inhibition efficiency of these compounds is as follows: 1> 2 > 3

3.4 Adsorption Considerations

In general, the adsorption of the inhibitor at the metal solution interface is the first step in the mechanism of inhibition in aggressive media. The surface coverage (θ) was calculated according to Eq. (1). A direct relationship between inhibition efficiency and the degree of surface coverage (θ) can be observed at different concentrations of the inhibitor in 1 M HCl. The polarization measurements were tested graphically for fitting Freundlich adsorption isotherm which can be expressed by the Eq. (4):

$$\log \theta = n \log C + \log K_{ads} \quad (4)$$

where C is the concentration of the inhibitor solution, n is the number of adsorption sites and K_{ads} is the adsorption equilibrium constant related to the free energy of adsorption ΔG^o_{ads}, Eq.(5) as

$$K_{ads}=1/55.5 \exp(-\Delta G^o_{ads}/RT) \quad (5)$$

where R is the universal gas constant, T is the absolute temperature. The value 55.5 is the concentration of water in the solution bulk in mol L^{-1}. By plotting values of log θ versus log C, linear plots were generated (Fig. 9). The Freundlich adsorption isotherm is better fit at 303K for carbon steel ($R^2 > 0.99$). This Figure indicates that the inhibitors obeyed Freundlich adsorption isotherm. The experimental data fitted with the Freundlich adsorption isotherm for the adsorption of investigated compounds on carbon steel were recorded in Table 5. The negative value of ΔG°_{ads} indicates that the adsorption process is spontaneous. It is well known that ΔG°_{ads} value up to -20 kJ mol^{-1} are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than - 40 kJ mol^{-1} involve sharing or transfer of electron from the inhibitor molecule to the metal surface to form a coordinate bond (chemisorption) [27]. The values of ΔG°_{ads} obtained are less than -20 kJ mol^{-1} indicating that the adsorption of these compounds on carbon steel surface in 1 M HCl solutions was physisorption.

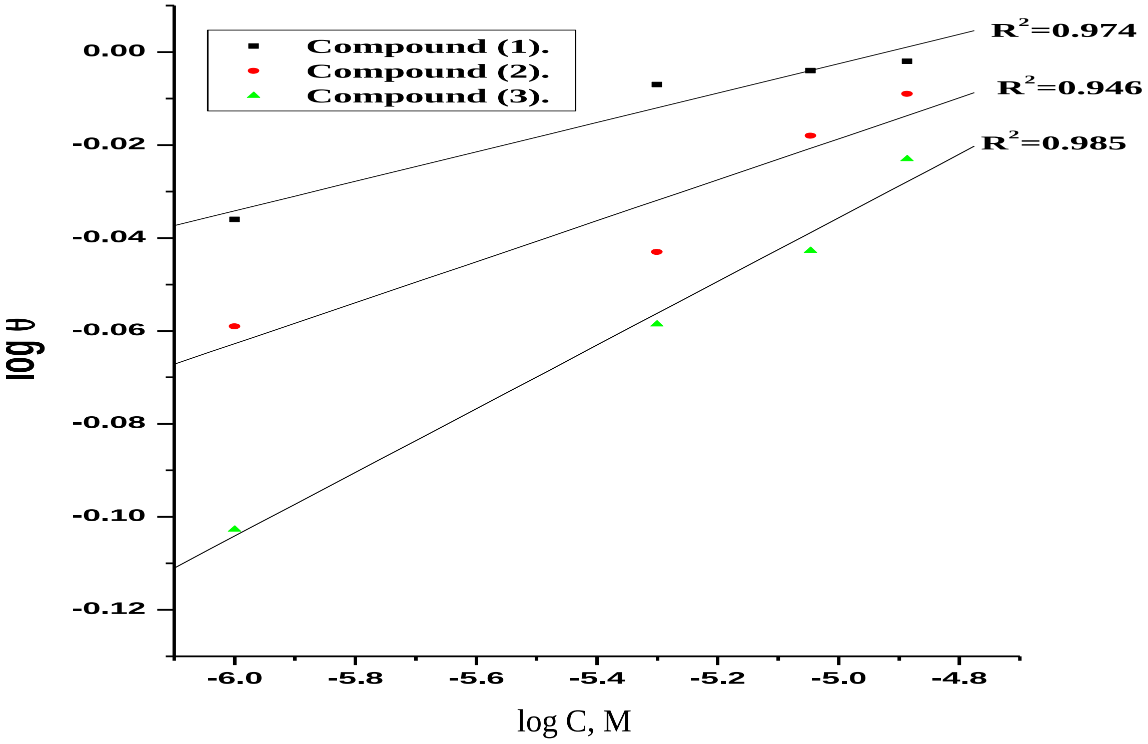


Figure 9. Curve fitting of corrosion data for carbon steel in 1M HCl in presence of different concentrations of organic additives to the Freundlich adsorption isotherm at 30°C

Table 5. Inhibitor equilibrium constant (K), free energy of adsorption ($\Delta G^o_{ads.}$) and number of active sites (n) for inhibitors additives at 30ºC

Inhibitor	Kinetic model		
	n	K_{ads}, M^{-1}	$-\Delta G^o_{ads.}$ kJ mol^{-1}
1	0.117	3.601	18.2
2	0.044	1.591	6.6
3	0.032	1.431	5.1

3.5 Effect of temperature

Energy of activation (E^*_a) has been calculated from Eq. (5) [30]:

$$\log \rho_2/\rho_1 = E_a/2.303R\,[1/T_1 - 1/T_2] \qquad (5)$$

where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2, respectively.

The values of the heat of adsorption (Q_{ads}) were calculated by the following equation [31].

$$Q_{ads} = 2.303\,R\,[\log(\theta_2 / 1 - \theta_2) - \log(\theta_1 / 1 - \theta_1)] \times [T_1 \,.\, T_2 / T_2 - T_1] \qquad (6)$$

where, θ_1 and θ_2 [$\theta = (i_{corr} - \overset{\circ}{i}_{corr})/i_{corr}$] are the fractions of the metal surface covered

The values given in Table (6) show that the E^*_a values are low (4.8 kJ mol^{-1}) in uninhibited acid whereas in inhibited acid they are higher. This suggests that the presence of reactive centers on the inhibitors can block the active sites for corrosion, resulting in an increase in E^*_a [28]. The higher value of activation energy (E^*_a) in the presence of inhibitor as compared to the activation energy in the absence of inhibitor in hydrochloric acid indicates that the inhibitor induces the energy barrier for the corrosion reaction, which leads to the decreasing of rate of corrosion of carbon steel in presence of inhibitor.

Table 6. Effect of temperature on corrosion rate (icorr), inhibition efficiency (% IE), energy of activation (E^*_a), and heat of adsorption (Q_{ads}) for carbon steel in 1 M HCl containing 11×10^{-6} M investigated inhibitors

Temp. K	298		308			
Inhibitor	$i_{corr,}$ µA cm^{-2}	θ	i_{corr} µA cm^{-2}	θ	$E^*_{a,}$ kJ mol^{-1}	$-Q_{ads}$ kJ mol^{-1}
Blank	637	------	990	-------	4.8	-----------
(1)	3.4	0.995	10.3	0.990	12.1	80.7
(2)	13.5	0.979	34.5	0.965	10.3	56.8
(3)	23.9	0.962	55.9	0.944	9.3	47.0

The activation energy in inhibited acid is ranging from 12.1 kJ mol^{-1} to 9.3 kJ mol^{-1}, which indicates that the inhibitors are adsorbed physically. According to Aiola and Damaskin [32, 33], the value of activation energy less than 80 kJ mol^{-1} and even smaller than 5 k $Jmol^{-1}$ represents physical adsorption. It was evident that in all cases, the Q_{ads} values were negative and ranging from –80.7 to –47.0 kJ mol^{-1}. Oguzie [29] explained that the negative values of Q_{ads} also signify that the degree of surface coverage decreased with rise in temperature.

3.6 Mechanism of corrosion inhibition

As known the inhibition efficiency process depends essentially on the electron density of the active centers. The subsequent step is to follow the effect of substituted group whether increase or decrease the inhibition efficiency through its effect on the active centers, i.e., electron donating or withdrawing groups, e.g., - OCH_3, -CH_3, -Cl. Three substituted groups investigated are located in p-position of phenyl ring with respect to the benzonitrile molecule derivatives. The inhibition of such derivatives was determined by using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) methods. The order of inhibition efficiency was found to decrease as follows: -OCH_3 > -CH_3 > -Cl. The inhibition efficiency was found to increase with increasing the concentration of the inhibitors. The nature of substituted group, whether electron donating (-OCH_3, -CH_3) or withdrawing (-Cl), reflects its effect on the inhibition efficiency. So, therefore, one can say that the -OCH_3 and –CH_3 groups increase the electron density of the active centers. Consequently, the inhibition efficiency increases. It follows that the -OCH_3 is more efficient than the -CH_3 group. From the structural point of view, both -CH_3 and OCH_3 groups have + R (mesomeric effect) but the inductive effect is + I and – I, respectively. Although the - CH_3 group has + R but its effect is very slight as result of hyperconjugation. In case of -OCH_3 group, the effect of + R is large and also the inductive effect (- I). The inhibition efficiency of - Cl group is the least one, due to its highest electrophilic character, so it comes the last among the additives used. Evidence for the validity of the above explanation is gathered from the application of Hammett constant σ, (σ OCH_3 = - 0.27, σ CH_3 = - 0.17, σ Cl = + 0.23).

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