



Inhibitive heteroamic acid behavior against 0.3N sulfuric acid corrosion of carbon steel

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ABSTRACT

The corrosion efficiency of a newly synthesized cefotaxime derivative with carbon steel was studied in 0.3N sulfuric acid. The results of potentiostatic polarization measurements demonstrated that this derivative is a good corrosion inhibitor. The inhibition in both of the corrosive media was observed to be a mixed type. The potential of zero charge (PZC) at the metal-solution interface was determined for both the inhibited and uninhibited solutions to provide the mechanism of inhibition. The inhibitor formed a film on the metal surface through chloride or sulfate bridges depending upon the medium. The temperature dependence of the corrosion rate was also studied in the temperature range from (35 - 65) °C.

Keywords: corrosion, sulfuric acid, carbon steel, β -lactam, pyromellitic dianhydride, amic acid.

INTRODUCTION

The β -lactam group; the four-membered nitrogen-containing ring; of antibiotics is one of the most important group of antibacterial agents used in clinical medicine. On the basis of the molecular structures surrounding and supporting this active site, they classified to four groups: cephalosporins, penicillins, carbapenems, and monobactams. Cephalosporins are the safest and the effective bactericidal agents esp. against gram-negative organisms and differ from penicillins by the heterocyclic ring system. [1]. Cefotaxime is an antimicrobial agent commonly used for severe Salmonella infections, especially in children [2] and has an excellent activity against most strains of *S. pneumoniae*, and high level resistance to penicillin [3].

Also, cefotaxime is considered as an excellent corrosion inhibitor by Shukla and Quarishi. They studied the corrosion inhibition of mild steel in 1 M HCl solution by cefotaxime sodium using Tafel polarization, electrochemical impedance spectroscopy and weight loss measurement. It was reported [4] to be more effective as corrosion inhibitor (95.8%) as a result of the presence of free NH_2 group which gets strongly protonated in hydrochloric acid solution without considering its instability of in acidic media [5]. The hydrolysis of cefotaxime sodium would be expected by either de-esterification or β -lactam cleavage at this low pH. [6].

Corrosion by its simplest definition is the process of a metal returning to the material's thermodynamic state which is electrochemical reaction that follows the laws of thermodynamics and it is time and temperature dependent. Corrosion in aqueous solutions is the most common of all corrosion processes [7].

Corrosion of metallic surfaces [7] can be controlled or reduced by the addition of chemical compounds to the corrodent. This form of corrosion control is called inhibition and the compounds added are known as corrosion inhibitors, which is one of the most common effective and economic methods to protect metals especially in acid media [8].

The majority of the well-known inhibitors are organic compounds containing heteroatom, such as O, N, or S and that, at the same time, contain N and S in their structures are of particular importance, since these provide an excellent inhibition compared with the compounds that contain only N or S [9].

The aim of this work is to study the corrosion inhibition efficiency of newly prepared cefotaxime –pyromellitic diamic acid with carbon steel against 0.3N sulfuric acid by Tafel polarization technique.

EXPERIMENTAL SECTION

Instruments and Chemicals:

Instruments: Atomic Absorption Spectrophotometer, Shimadzu. Japan. SpectroMax_x, stationary metal analyser, AMETEK Spectro-Analytical Instrument (Germany, 2012/model). Melting points were determined on Gallenkamp capillary melting point apparatus. FTIR spectra were recorded using KBr discs on Shimadzu FTIR-8400 Fourier Transform Infrared spectrophotometer.

¹H-NMR and ¹³C-NMR spectra were recorded on near magnetic resonance Bruker, Ultrashield 300 MHz in Jordan, using tetramethylsilane as internal standard and deuterated dimethyl sulfoxide (DMSO-d₆) as solvent.

Chemicals: all the used chemicals were from BDH and used without further purification.

Synthesis of N-(substituted) pyromellitic bisamic acid [10]

cyclic anhydride (pyromellitic anhydride) (0.01 mol) in (25mL) of acetone was added dropwise to a solution of (0.02mol) of a primary hetero-amino compound (cefotaxime) in (25mL) of acetone with stirring and cooling. Stirring was continued for four hours then the deep brown precipitated amic acid was filtered off, washed with diethyl ether, dried, and recrystallized from acetone. (Yield: 57%, m.p: > 300 °C). FTIR data (ν, cm⁻¹): 3444 and 3429 (OH) carboxylic and ν(NH), 1743 (C=O) ester, 1678 (C=O) carboxylic, 1647 (C=O) amide, 1627(C=N), 1570 (C=C) aromatic, 1261(C-O) ester, 678 (C-S) thiazole. ¹HNMR data (δ, ppm): =(2.7 (methyl), 2.85 (aliphatic), 3.9 (-CH₂O), 4.8 (OCH₃), 6 (vinylic), 7.1-7.9 (aromatic), 8.2-8.8 (NH), 12.55 (OH) protons. ¹³CNMR data (ppm): 30.7 (methyl), 34.2-36.8 (aliphatic), 56.5 (-CH₂O), 62.1-62.9 (OCH₃), 63.3-71.1 (vinylic), 131-135 (aromatic), (162-163 (C=N),), (166.4-166.6 (C=O) amide, 167.1 (C=O) carboxylic, 169.8-169.9 (C=O) ester carbons.

Carbon steel species preparation:

The circular carbon steel sheets of 2.5 cm x 0.02 cm were abraded with a series of emery paper (grade 320-500-800) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed at inclined position in beakers which contained 50 ml of the studied sulfuric acid concentration with different concentrations of the inhibitor.

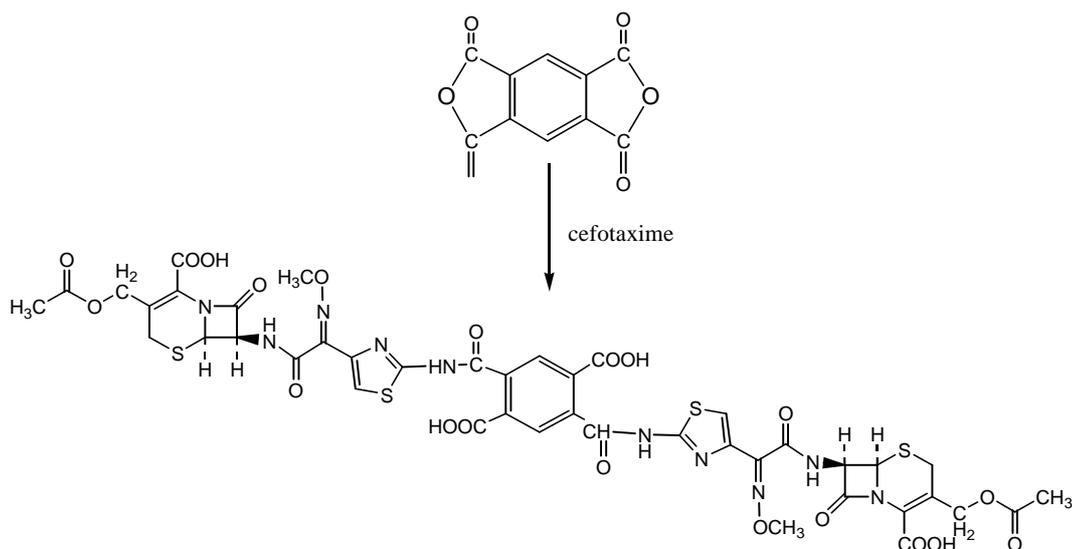
The aggressive acid solution (with or without inhibitor presence) was open to air. After a specific time, the specimens were taken out, washed, dried, and weighed accurately.

The material composition employed for the present work was characterized with two different instrumentations (Atomic Absorption Spectrophotometer and SpectroMax_x/ stationary metal analyser) to specify its actual metallurgical type: C% : 0.187, Si% : 0.311, Mn%: 1.03, S%: 0.012, Ni%: 0.029, Fe%: 98.3.

RESULTS AND DISCUSSION

Cefotaxime introduced in reaction with pyromellitic dianhydride producing new pyromellitamic acid containing different heterocycles.

The strategy in synthesis of new heterocyclic derivatives based on choosing known biologically active compound having wide application in pharmaceuticals and industrial uses (cefotaxime), introducing it in reaction with pyromellitic dianhydride. This reaction afforded characterized pyromellitamic acid which linked to cefotaxime moiety with FTIR, ¹HNMR, and ¹³CNMR spectroscopies as indicated in Scheme (1).



Scheme (1)

a. E_{corr} , i_{corr} , and P% results:

A convenient way to express the corrosion behaviour of a metal is by considering its potential – current density diagram which is generally known as the polarization curve (Figure (1)).

The corrosion potential (E_{corr}) of a material in a certain medium at a constant temperature is a thermodynamic parameter in which under the equilibrium potential (in opposite sign) of the cell consisting of the working electrode and the auxiliary electrode, the rate of anodic dissolution of working electrode material becomes equal to the rate of the cathodic process that takes place on the same electrode surface.

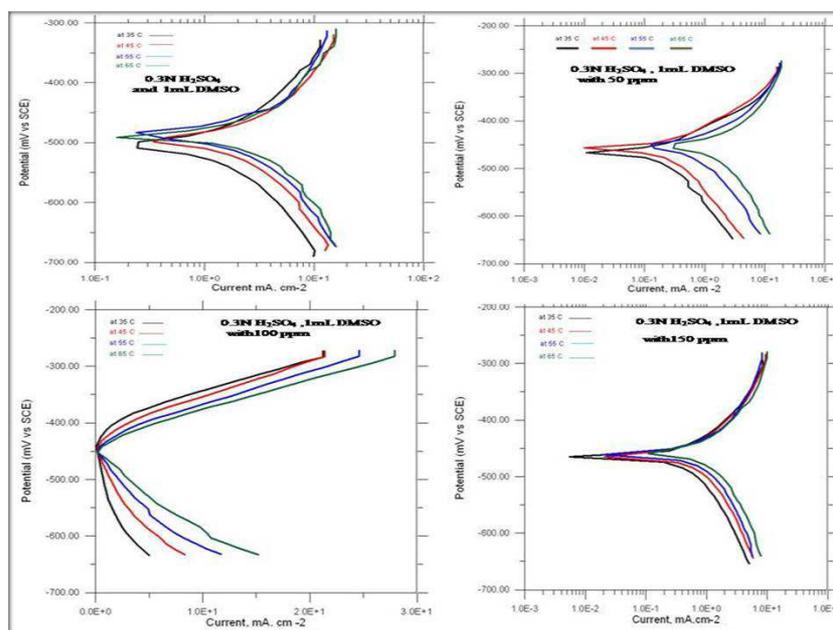


Figure (1): The polarization curve of carbon steel in 0.3N H_2SO_4 and different concentration of the prepared compound dissolved with 1mL DMSO at different temperatures

When (E_{corr}) becomes more negative, the potential of the Galvanic cell becomes more positive and the Gibbs free energy change (ΔG) for the corrosion process becomes more negative. The corrosion reaction is then expected to be more spontaneous on pure thermodynamic ground.

When the measured value of (E_{corr}) becomes less negative, the potential of the corresponding Galvanic cell becomes less positive, hence the (ΔG) value for the corrosion process becomes less negative, and the process is thus less spontaneous (Table (1)).

The corrosion current density (i_{corr}) is a kinetic parameter and represents the rate of corrosion under specified equilibrium condition. i_{corr} value for carbon steel in the applied acidic media without inhibitor is higher than with applied inhibitor which referred to its efficiency in general view (Table (1)).

Generally, the protection efficiency (P%), which was calculated from weight loss ($\text{g}/\text{m}^2 \cdot \text{d}$) data not from i_{corr} , was decreased with temperature increasing and may be affected with acid concentration, acid composition, and chemical structure of the tested inhibitor (Table (1), Figure (2)).

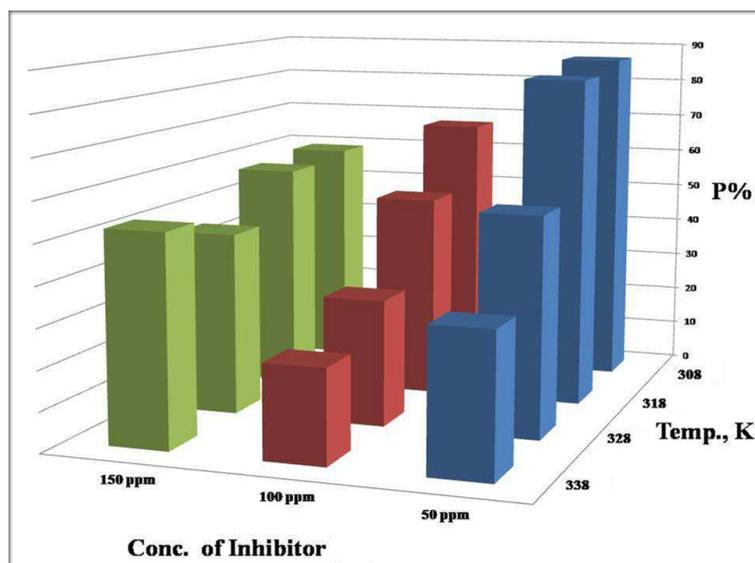


Figure (2): Comparison of inhibition efficiency of different concentration the prepared inhibitor for corrosion of carbon steel in 0.3 N H_2SO_4

Adsorption can be of a purely physical nature by means of electrostatic or Vander Waals forces, which are easily removed from the surface, or a chemical nature which forms chemical compounds.

Table (1): Values of the open circuit potential (OCP), the corrosion potential (E_{corr}), the corrosion current densities (I_{corr}), weight loss (wt loss), penetration loss, protection efficiency (P%), and Surface Coverage (θ) for carbon steel at three different concentrations of cefotaxime-amic acid derivative and four different temperatures in 0.3N sulfuric acid

Condition	Conc.	Temp., K	OCP, V	E_{corr} , V	I_{corr} , A/cm^2 ($\times 10^{-6}$)	Wt loss, $\text{g}/\text{m}^2 \cdot \text{d}^{-1}$	Penetration, mm. y	P%	θ
H_2SO_4 with 1 mL DMSO	0.3 N	308	-0.510	-0.5092	939.28	235.00	10.90	-	-
		318	-0.501	-0.4987	1320.00	330.00	15.30	-	-
		328	-0.494	-0.4855	1310.00	328.00	15.20	-	-
		338	-0.491	-0.4890	1730.00	432.00	20.10	-	-
76 with 1 mL DMSO and 0.3 N H_2SO_4	50 ppm	308	-0.468	-0.4656	125.02	31.30	1.45	86.6808	0.8668
		318	-0.459	-0.4562	210.62	52.70	2.44	84.0303	0.8403
		328	-0.459	-0.4496	590.51	148.00	6.85	54.8780	0.5487
		338	-0.458	-0.4577	1120.00	280.00	13.00	35.1851	0.3518
	100 ppm	308	-0.454	-0.4424	307.46	76.90	3.57	67.2765	0.6727
		318	-0.454	-0.4436	639.05	160.00	7.42	51.5151	0.5151
		328	-0.453	-0.4523	896.45	224.00	10.40	31.7073	0.3170
		338	-0.453	-0.4514	1330.00	331.00	15.40	23.3796	0.2337
	150 ppm	308	-0.475	-0.4641	385.12	96.30	4.47	59.0212	0.5902
		318	-0.465	-0.4659	559.27	140.00	6.49	57.5757	0.5757
		328	-0.462	-0.4606	706.19	177.00	8.20	46.0365	0.4603
		338	-0.460	-0.4575	819.18	205.00	9.51	52.5462	0.5254

They undergo a chemisorptions process which involves a charge sharing or a charge transfer process. This takes place more slowly than the physical adsorption, but the bonding achieved is stronger, making desorption considerably more difficult.

Inhibitor efficiency is higher for a compound which can donate electrons easily for the molecular site of adsorption and corresponds to high electron density at the presumed adsorption center in the molecular.

Most organic inhibitors are compounds with at least one polar function, the polar function is regarded as the reaction center for the establishment of the chemisorbed bond, whose strength is determined by the electron density of the atom acting as the reaction center⁽¹¹⁾.

A positive value of P% (Table (1)) indicates the inhibition of corrosion by the added inhibitors and it decreased with increasing in both its concentration and the applied temperature range. The variation in inhibitive efficiency with the concentration increasing of the acid may be attributed to the rate of evolution of hydrogen which may interfere with the absorption of the inhibitor on the metal surface.

b. The Tafel slope, transfer coefficient, and polarization resistance:

From deep analysis of the polarization curves which have been obtained for at four temperatures, it was possible to derive data concerning (the cathodic (β_c) and anodic (β_a) Tafel slopes) and (the cathodic (α_c) and anodic (α_a) transfer coefficients).

Values of α have been calculated from the corresponding values of the Tafel slope (β) using the relation⁽¹²⁾:

$$\alpha_c = 2.303RT / \beta_c F \quad \text{and} \quad \alpha_a = 2.303RT / \beta_a F$$

where R is the gas constant and F is the Faraday constant.

A value of the cathodic transfer coefficient α_c of ≈ 0.5 , or of the cathodic Tafel slope of ($-0.12 \text{ V.decade}^{-1}$), may be diagnostic of a proton discharge – chemical desorption mechanism in which the proton discharge is the rate – determining step.

If the chemical desorption is the rate – determining step, the rate would be independent of the overpotential since no charge transfer occurs in such a step and the rate becomes directly proportional to the concentration or the coverage (θ) of adsorbed hydrogen atoms⁽¹³⁾. On the other hand, if the discharge process is followed by a rate – determining step involving chemical desorption, the expected value of α should be (2.0).

The obtained results (Table (2)) indicated that the variation of the Tafel slopes and of the corresponding transfer coefficients could be interpreted in terms of the variation in the nature of the rate – determining step from charge transfer process to either chemical – desorption or to electrochemical desorption.

The obtained values of the (cathodic (β_c) and anodic (β_a) Tafel slopes) and (the cathodic (α_c) and anodic (α_a) transfer coefficients) were differed after the newly synthesized heterocyclic derivatives that indicated to their effects on the metal dissolution and subsequently the corrosion process at all (Table (2)).

The polarization resistance, R_p , according electrode, is defined as the slope of a potential (E) – current density (i) plot of the corrosion potential (E_{corr}) as:

$$R_p = \left(\frac{\partial \eta}{\partial i} \right)_{T,C} \quad \text{at } \eta \rightarrow 0$$

Where $\eta = E - E_{corr}$, is the extent of polarization of the corrosion potential and (i) is the current density corresponding to a particular value of (η). From the polarization resistance R_p , the corrosion current density i_{corr} can be calculated as :

$$i_{corr} = \beta / R_p$$

Where β is a combination of the anodic and cathodic Tafel slopes (β_a, β_c) as:

$$\beta = \beta_a \beta_c / 2.303 (\beta_a + \beta_c)$$

For the general case, by inserting (β) from the previous equation in ($i_{\text{corr}} = \beta / R_p$) equation one obtains the so-called the Stern – Geary equation⁽¹⁴⁾:

$$R_p = \beta_a \beta_c / (2.303 (\beta_a + \beta_c) i_{\text{corr}})$$

The measurement of polarization resistance has very similar requirements to the measurement of full polarization curves and it is particularly useful as a method to rapidly identifying corrosion up-setting and initiating remedial action⁽¹⁵⁾.

Table (2): Values of the Tafel slopes (β_a, β_c), transfer coefficients (α_a, α_b), polarization resistance (R_p), and equilibrium exchange current density for polarization carbon steel at three different concentrations of cefotaxime-amic acid derivative and four different temperatures in 0.3N sulfuric acid

Condition	Conc.	Temp., K	β_a , V. decade ⁻¹	β_c , V. decade ⁻¹	α_a	α_b	R_p , $\Omega \cdot \text{cm}^2 (\times 10^4)$	I_0 , A/ $\text{cm}^2 (\times 10^{-6})$
H ₂ SO ₄ with 1 mL DMSO	0.3 N	308	-0.1197	0.1277	0.5106	0.4786	0.0542	48.9561
		318	-0.1218	0.1117	0.5181	0.5649	0.0377	72.5290
		328	-0.1246	0.0954	0.5223	0.6822	0.0370	76.2616
		338	-0.1198	0.1254	0.5598	0.5348	0.0282	103.0396
76 with 1 mL DMSO and 0.3 N H ₂ SO ₄	50 ppm	308	-0.0975	0.0595	0.6268	1.0272	0.3724	7.1263
		318	-0.1283	0.0681	0.4918	0.9266	0.2165	12.6509
		328	-0.1494	0.0719	0.4356	0.9052	0.0761	37.1214
		338	-0.1248	0.0969	0.5374	0.6922	0.0408	71.2695
	100 ppm	308	-0.1565	0.0563	0.3905	1.0856	0.1438	18.4448
		318	-0.1587	0.0659	0.3976	0.9576	0.0694	39.4748
		328	-0.1264	0.0774	0.5149	0.8409	0.0504	56.0174
		338	-0.1336	0.0829	0.5020	0.8091	0.0339	85.8137
	150 ppm	308	-0.1309	0.0888	0.4669	0.6883	0.1205	22.0234
		318	-0.1303	0.1139	0.4843	0.5540	0.0833	32.8932
		328	-0.1425	0.1141	0.4567	0.5704	0.0652	43.3332
		338	-0.1315	0.1151	0.5100	0.5827	0.0558	52.1501

The term ($E_{\text{corr}} / i_{\text{corr}}$) corresponds to the resistance (R) of the metal/solution interface to charge – transfer reaction. It is also a measure of the resistance of the metal to corrosion in the solution in which the metal is immersed. The reaction resistance (R_p), which mainly depends upon the equilibrium exchange current density (i_0) determines what may be termed the polarizability, i.e., what overpotential ($\eta = E - E_{\text{corr}}$) a particular current density needs (for a driven cell) or produces (for a spontaneously performing cell).

The results of the polarization resistance (R_p) (calculated from term ($E_{\text{corr}} / i_{\text{corr}}$)) for the corrosion of carbon steel. For all applied condition, R_p decreased with temperature range increasing. The decreased of R_p values imply increasing corrosion rate (Table (2)).

c. Thermodynamic results:

Thermodynamics, the science of energy changes, has been widely applied to corrosion studies for many years. The change in free energy (ΔG) is a direct measure of the work capacity or maximum electric energy available from a system. Chemical and corrosion reactions behave in exactly the same fashion.

Thermodynamic laws tell us that there is a strong tendency for high energy state in a system to transform into low energy state. It is this tendency of metals to recombine with components of the environment that leads to the phenomenon known as corrosion⁽¹⁶⁾.

The free – energy change accompanying an electrochemical reaction can be calculated by the following equation⁽¹⁶⁾:
 $\Delta G = - nFE$

where ΔG is the free – energy change, n is the number of electrons involved in the reaction, F is the Faraday constant, and E equals the cell potential ($E = E_{\text{corr}}$).

From the value of ΔG at several temperatures, the change in the entropy (ΔS) of corrosion process could be derived according to the well – known thermodynamic relation:

$$\Delta S = - d(\Delta G) / dT$$

Values of ΔG are usually plotted against temperature (T); thus at any temperature the value of $[s - d(\Delta G)/dT = \Delta S]$ which corresponds to the slope of the $(-\Delta G)$ versus (T) plot at that temperature.

The change in free energy, ΔG , is related to ΔH , the change in the enthalpy, and ΔS , the change in entropy of the corrosion reaction at a constant temperature, T, by the equation ⁽¹⁶⁾:

$$\Delta G = \Delta H - T \Delta S$$

When a metal undergoes corrosion, there is a change in Gibbs free energy (ΔG) of the system, which is equal to the work, associated with the corrosion reaction.

The variation of the $(-\Delta G)$ for corrosion of carbon steel in the research conditions, generally values of ΔG were negative suggesting the existence of thermodynamic feasibility for the corrosion of the electrodes materials in the absence or the presence of the applied inhibitor in the acidic medium (Table (3)).

Values of (ΔS) were positive or negative depending on the positive or negative dependencies of (ΔG) values on temperatures. Values of (ΔS) reflect the change in the order and orientation of the solvent molecules around the hydrated metal ions in the corrosion medium when metal atoms were corroded and subsequently hydrated in the solution.

Table (3): The thermodynamic quantities for carbon steel at three different concentrations of cefotaxime-amic acid derivative and four different temperatures in 0.3N sulfuric acid

Condition	Conc.	Temp., K	- ΔG , KJ/mol	ΔS , KJ/mol. K	ΔH , KJ/mol
H ₂ SO ₄ with 1 mL DMSO	0.3 N	308	98.26032	0.142	54.52432
		318	96.23414		51.07814
		328	93.68694		47.11094
		338	94.36233		46.36633
76 with 1 mL DMSO and 0.3 N H ₂ SO ₄	50 ppm	308	89.84683	0.058	71.98283
		318	88.03291		69.58891
		328	86.75931		67.73531
		338	88.32237		68.71837
	100 ppm	308	85.36993	0.068	106.3139
		318	85.60149		107.2255
		328	87.28033		109.5843
		338	87.10666		110.0907
	150 ppm	308	89.55738	0.048	74.77338
		318	89.90472		74.64072
		328	88.88198		73.13798
		338	88.28378		72.05978

Values of ΔS were generally positive due to negativity of ΔG , this suggests a lower order in the solvated states of the metal ions as compared with the state of metal atoms in the crystal lattice of the corroding electrodes. The obtained results indicate the variation of (ΔS (KJ/mol. K)) with the absence and presence of the applied inhibitor (Table (3)).

Values of the enthalpy of corrosion (ΔH) reflect the enthalpy changes associated with the corrosion reaction and may be ranged from negative to positive values, according to the experimental conditions, indicating exothermic or endothermic nature of corrosion reaction.

ΔH values variation with changing of inhibitor concentration controlled by the all applied conditions. Generally, the direction of ΔH variation sequence is opposite to ΔG variation (Table (3)).

d. Kinetic of Corrosion:

The rate (r) of corrosion in a given environment is directly proportional with its corrosion current density (i_{corr}) in accordance with the relation ⁽¹⁶⁾ :

$$r = 0.13 (e / \rho) i_{\text{corr}}$$

where (e) is the equivalent weight of the metal and (ρ) is its density. For the increasing values of (i_{corr}) with a temperature follow Arrhenius equation ⁽¹⁷⁾, it is reasonable as:

$$\log (i_{\text{corr}}) = -E_a / 2.303 RT + \log A$$

where A and E_a are the pre-exponential factor and energy of activation of the corrosion process respectively.

Values of E_a were derived from the slopes of the $(\log i_{\text{corr}})$ versus $(1/T)$ linear plots while those of (A) were obtained from the intercepts of the plots at $(1/T=\text{zero})$; values of (A) , expressed in term of (Amper. cm^{-2}) , have then been converted into $(\text{molecules per cm}^2 \text{ per second})$, (A) was defined as:

$$A = (KT/h) \exp (\Delta S^* / R)$$

where K , h , T , R , ΔS^* are Boltzmann constant $(1.381 \times 10^{-23} \text{ J.K}^{-1})$, Planck constant $(6.62608 \times 10^{-34} \text{ J.S})$, temperature on Kelvin scale, gas constant (8.314 J/Mol. K) and the entropy of activation respectively.

In order to calculate the activation parameters⁽¹⁸⁾ of the corrosion process, transition state equation were used with Arrhenius equation:

$$i_{\text{corr}} = (RT / Nh) \exp (\Delta S^* / R) \exp (-\Delta H^* / RT)$$

where A is the pre-exponential factor; N , h are Avogadro's number and Plank's constant respectively and E_a , ΔH^* and ΔS^* are the activation energy, change in enthalpy and change in the entropy of the corrosion process. Straight lines are obtained with a slope of $-\Delta H^*/R$ and an intercept of $(\ln (R/Nh) + \Delta S^*/R)$ from which the values of ΔH^* and ΔS^* are calculated (Table (4)).

The apparent activation energy reflects on the difficulty of the reaction and denotes the energy barrier for the chemical reaction where lower E_a means lower energy barrier for the steel corrosion⁽¹⁹⁾.

The relationship existed between values of the activation energy (E_a) and logarithm of pre – exponential factor ($\log A$) in different media suggesting the operation of a compensation effect in kinetics of corrosion. This suggests that, the corrosion reaction proceeds on surface sites, which were associated with different energies of activation.

Generally, E_a values for inhibited solution are higher than the value for inhibitor-free solution. The increase in activation energy in the presence of inhibitors signifies physisorption⁽²⁰⁾.

However, in which the higher value of E_a for the inhibited system indicates physical adsorption in the initial stage, cannot be taken into account as decisive because of competitive inhibitor adsorption on the metal surface with water, whose desorption from the surface requires some activation energy⁽²¹⁾.

Therefore, the adsorption phenomenon of organic inhibitor molecules on the metal surface is not considered only as physical or chemical adsorption⁽²⁰⁾.

The positive sign of ΔH^* suggests that the dissolution process is endothermic in nature and its dissolution is slow⁽²²⁾. In the presence of tested compounds, E_a and ΔH^* values change in a similar manner. These results verify the known thermodynamic relationship^(23, 24) between E_a and ΔH^* :

$$(\Delta H^* = E_a - RT)$$

Typically, the enthalpy of physisorption process is lower than that of 40.00 kJ/mol while the enthalpy of chemisorptions process approaches 100 kJ/mol ⁽²⁵⁾.

Generally, the values of ΔS^* are higher for inhibited solutions than for uninhibited solution. This might be the result of the molecular adsorption, which could be regarded as a semi-substitution process between the molecules in the aqueous phase and water molecules on the carbon steel surface⁽²⁰⁾.

The molecular structure is one of the major factors influencing the adsorption of the organic molecules on the metal surface, and hence the inhibitor properties, especially in the case of chemisorption, which involves charge sharing or charge transfer from the inhibitor molecules to the metal to form coordinate type of bonds. The electronic density of the atoms, acting as reaction centers of the molecules, determines the adsorption bond.

So the influence of the chemical structure is limited to the molecular area in the adsorbed state, because it determines the area of the metal, shielded by the inhibitor.

Owing to the acidity of the medium ⁽²⁶⁾, the N, O, and S heteroatom could not remain in solution as free acids or bases. They exist as a neutral species or in the cationic form. Thus, the adsorption of the examined molecules could be occurred due to the formation of a links between the d-orbital of iron atoms, involving the displacement of water molecules from the metal surface, and the lonely sp^2 electron pairs present on the N, O, S atoms of the heterocyclic rings.

Moreover, these compounds may also adsorb through the electrostatic interactions between the positively charged nitrogen atom and the negatively charged metal surface.

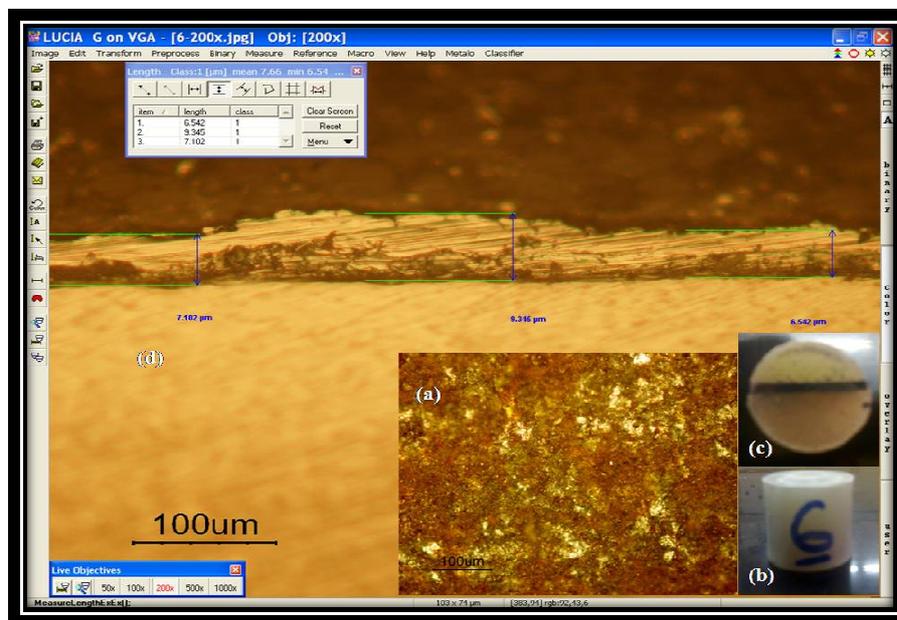


Figure (3): Optical Microscope images of (0.3N) sulfuric acid and 1mL DMSO after potentiostatic test: (a) general view (100µm), (b) in polymethyl methacrylate, (c) upper view after cross section operation, (d) cross section image



Figure (4): Optical Microscope images of (50 ppm) after potentiostatic test (general view (100µm))

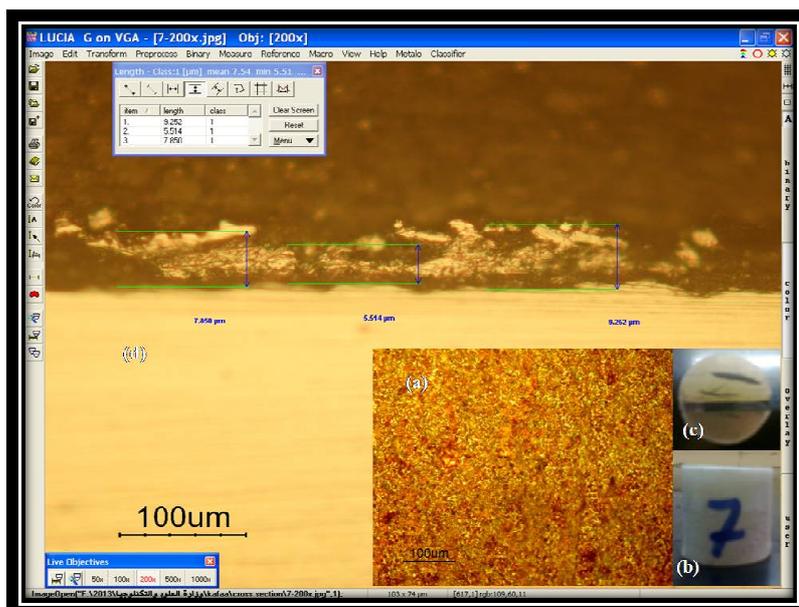


Figure (5): Optical Microscope images of (100 ppm) after potentiostatic test: (a) general view (100µm), (b) in polymethyl methacrylate, (c) upper view after cross section operation, (d) cross section image

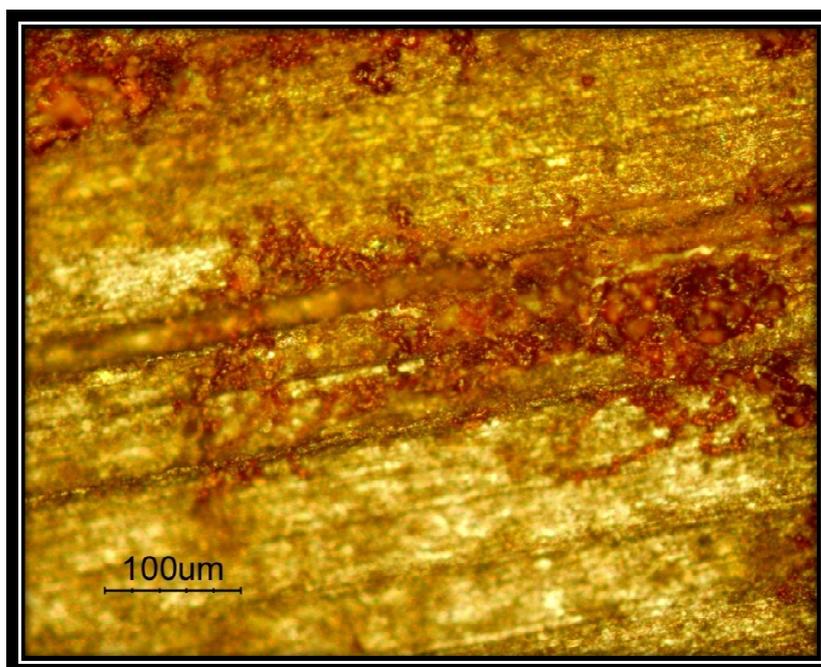


Figure (6): Optical Microscope images of (150 ppm) after potentiostatic test (general view (100µm))

The better performance of the tested compounds in acidic solutions can be related to the specific adsorption of anions having a smaller degree of hydration. Being specifically adsorbed, they create an excess negative charge toward the solution and favor more adsorption of the cations.

The high p-electron density of the heterocyclic moiety comes from the high electronegativity of its oxygen heteroatom in addition to the presence of electron donating group which attached directly to the heterocyclic moiety. This in turn leads to decrease the positive charge density on the cationic form of the moiety, causing decrease of the inhibition effect.

The lowest inhibition efficiency⁽²⁶⁾ may be a result to the absence of the positive charge. This should be attributed to the difficulty of resonance to take place in the acid medium. Moreover, the small size of compound may result in low surface coverage and consequently leading to less inhibition effect.

When the inhibitor contains carboxylic acid group, this group can react with corrosion products, which increases the protective layer thickness. This leads to slightly better corrosion inhibition.

In the uninhibited H₂SO₄ solutions, the mechanism of anodic dissolution involves successively the reversible adsorption of the anions (SO₄²⁻) to the surface, release of electrons from the adsorbed anions to the metal surface and desorption of the adsorbed anions along with Fe⁺² ions, after picking up electrons from the Fe atoms^(27,28).

Table (4): Kinetic quantities for carbon steel at three different concentrations of cefotaxime-amic acid derivative and four different temperatures in 0.3N sulfuric acid

Condition	Conc.	Temp., K	E _{as} , KJ/mol.	A, Molecules/ cm ² .s	ΔS*, KJ/mol. K	ΔH*, KJ/mol.
H ₂ SO ₄ with 1 mL DMSO	0.3 N	308	15.8232	2.9463 x 10 ¹⁸	0.2376	13.1406
		318				
		328				
		338				
76 with 1 mL DMSO and 0.3 N H ₂ SO ₄	50 ppm	308	65.7512	1.0029 x 10 ²⁶	0.3818	63.0706
		318				
		328				
		338				
	100 ppm	308	41.1089	1.9736 x 10 ²²	0.3109	38.4283
		318				
		328				
		338				
150 ppm	308	21.7128	1.2197 x 10 ¹⁹	0.2494	19.0456	
	318					
	328					
	338					

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