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A Pharmaceutically Active Compound as Corrosion Inhibitor for Carbon Steel in Acidic Medium: Electrochemical and Thermodynamic Studies

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ABSTRACT

The inhibitive action of pharmaceutically active compound on corrosion of carbon steel (CS) in 1.0 M HCl was studied by weight loss, potentiodynamic polarization and Electrochemical impedance spectroscopy techniques. Effect of temperature was investigated at temperature range (303-333 K). The obtained results indicate that the examined compound is an excellent inhibitor in 1.0 M HCl, and the inhibition efficiency (η %) increases with increasing the inhibitor concentration while it decreases with rising the temperature solution. Polarization curves show that the studied drug is mixed-type inhibitor in acidic medium. The adsorption of the inhibitor on the CS surface obeys the Langmuir adsorption isotherm. Thermodynamic parameters have been calculated and discussed. Surface analysis was performed to emphasis the inhibition efficiency of the studied drug inhibitor.

Keywords: Corrosion inhibitor, thermodynamic, carbon steel, Pharmaceutical compound.

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INTRODUCTION

The corrosion of metals has received prime attention of material scientists and chemists since it has many serious adverse effects including economic, health, safety, technological, and cultural consequences. Carbon steel Corrosion is one of the major areas of concern in many industries, where acids are widely used for application such as acid pickling, acid de scaling, and oil well acidizing [1]. The corrosion of steel in such environments and its inhibition constitute a complex problem of processes [2]. So, nowadays the study of carbon steel corrosion phenomena has become an important industrial and academic topic [3,4].

The use of inhibitors is one of the most practical methods for protection metal against corrosion, especially in acidic media [5]. Among various acid organic inhibitors, N-heterocyclic compounds are considered to be the most effective corrosion inhibitors [6]. However, due to the toxicity of widely used corrosion inhibitors and the ever tightening environmental regulations surrounding their use and disposal, there is great interest in replacing harmful inhibitors with effective non-hazardous alternatives. Over the past two decades, extensive research and development have led to the discovery of new classes of corrosion inhibitors, and the importance on the use of several drugs as corrosion inhibitors has grown [7-9].

The inclination towards eco-friendly corrosion inhibitors development intersects across several goals of pharmaceutical research, one of which is to discover or develop molecules with desired biological activity. Efforts to attain this goal are strongly driven by the notion of molecular similarity because in general, similar molecules tend to behave similarly [10]. Assigning an unknown molecule to the class of active or inactive molecules using an inter-molecular similarity measure is known as virtual screening [11], and has already been emerged as a method to accelerate the discovery process of potential corrosion inhibitors [12]. The inhibitive effect of four antibacterial drugs, namely ampicillin, cloxacillin, fluclocoxcillin, and amoxicillin towards the corrosion of aluminum was investigated [13].

The studied drug inhibitor belongs to cephalosporins , which are a major group of semi-synthetic β-lactam antibiotics used in clinical medicine for treatment of bacteria-related infections. They are closely related in fundamental structure and antibactericidal action mechanism to penicillins. They are used for the treatment of infections caused by both gram-negative and gram-positive bacteria. Cephalosporins are among the oldest and most frequently prescribed naturally occurring antimicrobial agents, Among these cephalosporins, only for the present, cefatrexyl, cefazolin and cefalexin are used as corrosion inhibitors of iron in acidic media [14, 15]. The inhibition action of these drugs was attributed to blocking the surface via formation of insoluble complexes on the metal.

The objective of the present work is to gain some insight into the inhibitive effect of the selected antibacterial drug toward the corrosion of carbon steel in 1.0 M HCl solution by performing several techniques. The effect of temperature was also studied. Several isotherms were tested for their relevance to describe the adsorption behavior of the compound studied.

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MATERIALS AND METHODS

Experimental

Materials

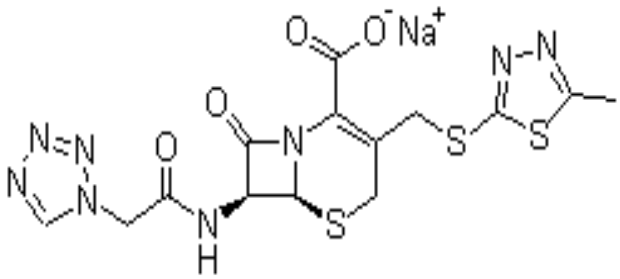

Fig.1- Molecular structure of examined antibacterial drug.

Tests were performed on carbon steel having composition (wt. %) C = 0.13, Mn = 0.48, Si = 0.014, S = 0.025, P = 0.014 and the remainder being Fe. The used inhibitor is an antibacterial drug, it is available under the brand name zinol powder injection (m.p. 470 K); zinol is the commercial name of (6R, 7R)-3-{[(5-methyl-1, 3, 4-thiadiazol-2-yl) thio] methyl}-8-oxo-7- [(1H-tetrazol-1-ylacetyl) amino]-5-thia-1-azabicyclo [4.2.0] oct-2- ene-2-carboxylic acid. It is a first generation cephalosporin antibiotic. Fig.1 shows the molecular structure of the studied anti bacterial drug. The stock solution of the pharmaceutically active compound was diluted to a certain concentration of the effective substance. The inhibitor concentration range used in the weight loss and electrochemical studies was 5 x10^{-5} M to 60 x 10^{-5} M. The aggressive solutions, 1.0 M HCl, were prepared by dilution of AR grade 37% HCl in distilled water.

Weight loss measurements

The carbon steel sheets of 6 cm x 2.5 cm x 0.5 cm have been abraded with a series of emery papers (grade 320, 500, 800, and 1200) and then washed with distilled water and acetone. After weighing accurately (using Mettler AG104 0.1 mg Analytical Balance), the specimens were immersed in 150 ml beaker, which contained 100 ml hydrochloric acid with and without addition of different concentrations of the tested inhibitor. After immersion, the specimens were taken out, washed, dried, and weighed accurately [16]. The tests were repeated at different temperatures of 303, 313,323 and 333 K. The corrosion rate (R) and the inhibition efficiency (η %) were calculated from the following equations :

$$R = W/St \quad (1)$$

$$\eta\ \% = [(R_o - R)/R_o] \times 100 \quad (2)$$

where, W is the average weight loss of three parallel carbon steel sheets, S the total surface area of the specimen, t is immersion time (6 h), R_o and R are the values of the corrosion rate without and with addition of the inhibitor, respectively .

Electrochemical measurements

Electrochemical measurements have been carried out in a conventional three-electrode cell configuration in which carbon steel was used as working electrode, saturated calomel electrode (SCE)

and a platinum wire as reference and auxiliary electrodes, respectively. Before each test, the working electrode was immersed in test solution and the change in open circuit potential (E_{ocp}) of carbon steel versus SCE reference electrode was recorded as a function of exposure time for 30 min. After recording E_{ocp-t}, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization measurements were performed, consecutively.

Electrochemical impedance spectroscopy measurements were carried out using A Radiometer Voltalab Master 40 Type PGZ 301 Fitting with analysis program Zsimpwin. Impedance spectra were obtained in the frequency range between 100 kHz and 50 mHz using 10 steps per frequency decade at corrosion potential after 30 min. of immersion in 1.0 M HCl solution without and with different concentrations of the studied inhibitor. AC signal with 10mV amplitude peak to peak was used to perturb the system. EIS diagrams are given in the Nyquist representation.

The electrochemical polarization measurements were measured by Potentiodynamic Polarization Radiometer Voltalab master potentiostat model (Voltalab Master 40 Type PGZ 301). Polarization curves were recorded potentiodynamically, at the scan rate of 2mV/s, in the range of -1000 to -300 mV versus OCP.

Surface film characterization

Carbon steel coupons were immersed in 1M HCl for 48 hrs in absence and presence of optimum concentration of the studied inhibitor. The corrosion products developed on the surface of the coupons were taken up, gently powdered and homogenized. The identification of the phases was carried out using using X-ray powder diffractometer, X'PERT PRO MPD (PANalytical, Netherland). The XRD patterns were recorded with a Cu Kα radiation of wavelength of 1.5406 A^o operated at 40 kV/40 mA.The samples were step-scanned in the 2θ range of 4^o-80^o with a step size 0.02 and a time step of 0.4s. The individual crystalline phases formed on the carbon steel surface were identified using the ICDD-PDF database.

EDX analysis was performed with energy dispersive spectrometer conjugated with Jeol 5400 scanning electron microscope (SEM). Prior to analysis, the carbon steel specimens have been kept immersed in 1.0 M HCl solution for 48 h in the absence and presence of 60 x 10^{-5} M of the inhibitor. Finally, the specimens have been washed thoroughly and submitted to 5 min of ultrasonic cleaning in order to remove loosely adsorbed ions.

RESULTS AND DISCUSSION

Weight loss measurements

Effect of inhibitor concentration

The values of corrosion rates and inhibition efficiencies obtained from weight loss measurements using different concentrations of the studied drug inhibitor in 1.0 M HCl at various temperatures are presented in Table 1. The data reported in the table reveals that corrosion rate values decrease as the concentration of inhibitor increases. Consequently, percent inhibition efficiency values increase with the increase in the concentration. This behavior could be attributed to the strong interaction of compound with the metal surface that results in the adsorption of inhibitor molecules [17].The lone pair of electron on the nitrogen atoms will co-ordinate with the metal atoms of actives sites. Also, the presence of higher electron density in drug molecule causes stronger interaction with

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metal surface. The nitrogen atoms can donate π electrons to the metal surface to increase adsorption and hence improves the inhibition process of the corrosion [18].

Table 1. Corrosion parameters obtained from weight loss measurements of carbon steel in 1.0 M HCl containing different concentrations of drug inhibitor at different temperatures.

Inhibitor Conc. (M x 10^{-5})	Temperature (K)	Corrosion Rate (mg cm^{-2} h^{-1} x10^{-2})	I.E (%)
Blank	303	7.84	-
	313	8.60	-
	323	9.60	-
	333	10.0	-
5	303	1.9	76
	313	3.4	60
	323	4.6	48
	333	6.4	39
10	303	1.6	80
	313	2.7	69
	323	3.6	62
	333	4.8	54
20	303	0.9	88
	313	1.9	79
	323	2.8	71
	333	3.7	64
40	303	0.5	94
	313	1.5	83
	323	2.4	75
	333	3.0	71
60	303	0.3	97
	313	1.2	86
	323	2.1	78
	333	2.7	75

Effect of temperature

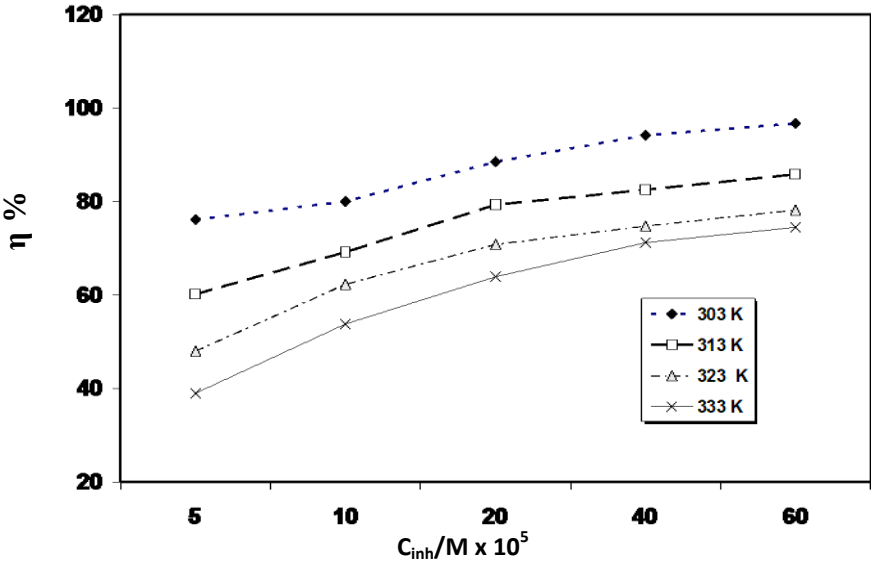

Fig. 2.Evolution of inhibition efficiency of various concentrations of drug inhibitor at different temperatures.

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The influence of temperature on the corrosion behavior of carbon steel in 1.0M HCl with and without different concentrations of the studied inhibitor is investigated by weight loss trends in the temperature range 303-333 K. The variation of inhibition efficiency of the drug inhibitor with temperature is shown in Fig. 2, it can be seen that inhibition efficiency decreases with increasing temperature, which indicates desorption of inhibitor molecules [19].

Adsorption isotherm

Adsorption isotherms are usually used to describe the adsorption process. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clues to the nature of the metal- inhibitor interaction. Adsorption of the organic molecules occurs as the interaction energy between molecule and metal surface is higher than that between the H_2O molecule and the metal surface [20]. For this purpose, the values of surface coverage (θ), defined by IE /100, for different concentrations of drug inhibitor in 1.0 M HCl in the temperature range (303–333 K) were calculated from weight loss data to explain the best isotherm to determine the adsorption process from the experimental data obtained.

Fig.3 shows the relationship between $C_{inh.}$ /θ and $C_{inh.}$ at the studied temperature range. The best fitted straight line is obtained for the plot of C_{inh}/ θ versus C_{inh} with slopes around unity. The correlation coefficient (r^2) was used to choose the isotherm that best fit experimental data. This suggests that the adsorption of the drug inhibitor on metal surface followed the Langmuir adsorption isotherm as shown in Fig. 3. By far, the experimental data were best fitted by Langmuir" adsorption isotherm equation [21]:

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \qquad (3)$$

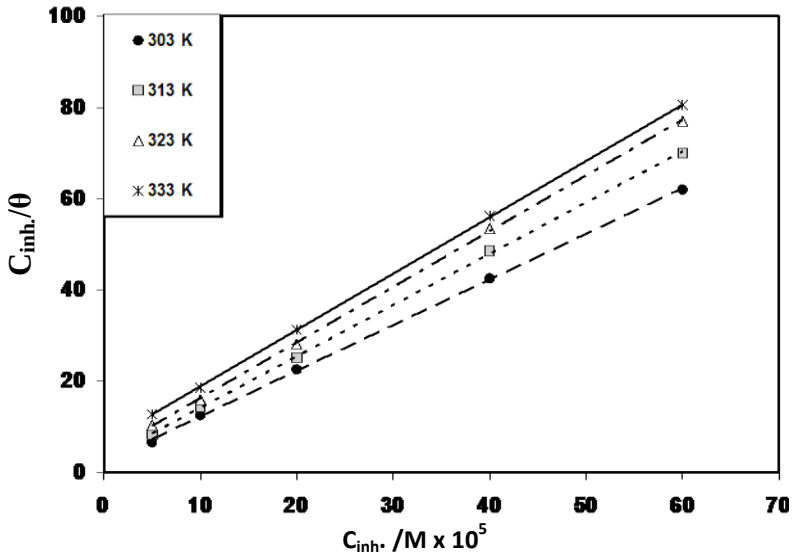

Fig.3.Langmuir adsorption plots for carbon steel in 1.0 M HCl at different temperatures.

Where, K_{ads} is the equilibrium constant of the adsorption process. This isotherm assumes that adsorbed molecules occupy only one site and it does not interact with other adsorbed species.

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The K_{ads} values can be calculated from the intercept lines on the $C_{inh.}$ /θ axis. K_{ads} is related to the standard free energy of adsorption (ΔG^{o}_{ads}) with the following equation [14]:

$$\Delta G^{o}_{ads} = -RT \ln (55.5\ K_{ads}) \qquad (4)$$

Where, R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/L. The calculated values of $K_{ads.}$ and ΔG^{o}_{ads} are given in Table 2.

Table 2 Thermodynamic parameters for the adsorption of drug inhibitor on carbon steel in 1.0 M HCl at different temperatures.

Temperatures, (K)	$K_{ads.}$ (mol^{-1})	Slope	r^2	ΔG^{o}_{ads}, ($kJmol^{-1}$)	ΔH^{o}_{ads}, ($kJmol^{-1}$)	ΔS^{o}_{ads}, ($Jmol^{-1}$)
303	45327	1.0013	0.9997	-37.1	-29.5	25.1
313	33924	1.1234	0.9997	-37.6	-29.5	25.9
323	24565	1.2203	0.9998	-37.9	-29.5	26.0
333	15345	1.2357	0.9999	-37.8	-29.5	24.9

Generally, the magnitude of ΔG^{o}_{ads} around −20 kJ/mol^{-1} or less negative indicates electrostatic interactions between inhibitor and the charged metal surface (i.e., physisorption). Those around −40 kJ/mol^{-1} or more negative are indicative of charge sharing or transferring from organic species to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions). In the present work, the calculated values of ΔG^{o}_{ads} at 303 K for carbon steel around −37 kJ/mol^{-1}, which indicated that adsorption of the studied inhibitor molecules on the metal surface involves complex interactions: both physical and chemical process [14]. The negative value of ΔG^{o}_{ads} indicates spontaneous adsorption of the inhibitor on the metal surface.

The enthalpy of adsorption can be calculated from the rearranged Gibbs-helmholtz equitation [22]:

$$\Delta G^{o}_{ads}/T = \Delta H^{o}_{ads}/T + K \qquad (5)$$

The variation of $\Delta G^{o}_{ads}/T$ with 1/T gives a straight line with a slope that equals ΔH^{o}_{ads} (Fig. 4). It can be viewed from the Figure that $\Delta G^{o}_{ads}/T$ decrease with 1/T in a linear manner. The calculated values are shown in Table 2.

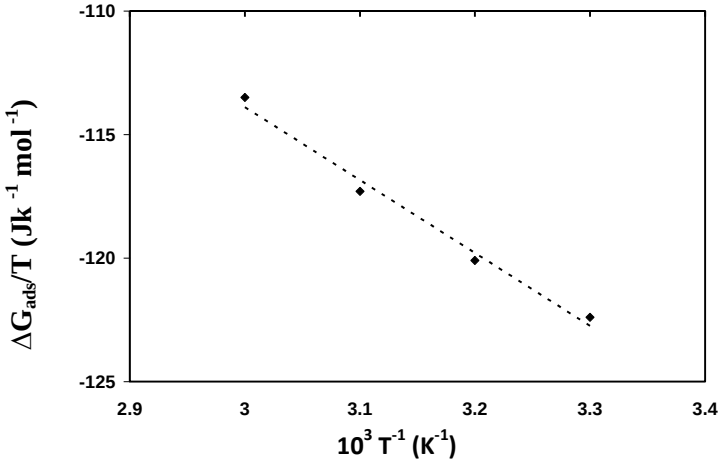

Fig. 4. Variation of $\Delta G^{o}_{ads}/T$ versus T on carbon steel in 1.0 M HCl containing drug inhibitor.

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The adsorption heat could be approximately regarded as the standard adsorption heat under experimental conditions [22]. The negative sign of ΔH^{o}_{ads} in HCl solution indicates that the adsorption of inhibitor molecule is an exothermic process.

Generally, an exothermic adsorption process signifies either physisorption or chemisorption while endothermic process is recognized to chemisorption [23]. Typically, the enthalpy of physisorption process is lower than 41.86 kJ mol l^{-1} while the enthalpy of chemisorption process approaches 100 kJ mol l^{-1} [24]. In the present study, the absolute value of enthalpy is −29.5 kJ mol^{-1}, which is intermediate case. Then the standard adsorption entropy ΔS^{o}_{ads} (Table 2) was obtained using the thermodynamic basic equation:

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T\Delta S^{o}_{ads} \qquad (6)$$

The positive values of ΔS^{o}_{ads} in the presence of inhibitor indicate that the adsorption is a process accompanied by increase in entropy. These results can also be interpreted with increase of disorders due to the increase in the number of water molecules which can be desorbed from the metal surface by one inhibitor molecule. Therefore, it is revealed that decrease in the enthalpy is the driving force for the adsorption of the inhibitor on the surface of the metal [25].

Thermodynamic parameters

The values of thermodynamic parameters can provide valuable information about the mechanism of corrosion inhibition. The thermodynamic functions for dissolution of carbon steel in the absence and in the presence of various concentrations of the studied inhibitor were obtained by applying the Arrhenius equation and the transition state equation [22, 26]:

The apparent activation energy (E^{o}_{a}) of metal dissolution in acid media can be calculated from the Arrhenius equation (27):

$$\ln C_R = - E^{o}_{a}/RT + A \qquad (7)$$

Where, R is the universal gas constant; A is the Arrhenius pre-exponential factor, and T is the absolute temperature. The values of E^{o}_{a} obtained from the slope of the ln C_R versus 1/T plot (Fig.5) are given in Table 3.

Table 3 Activation parameters for carbon steel in 1.0 M HCl in the absence and presence of different concentration of the inhibitor.

Inhibitor Conc./ M x 10^{-5}	E^{o}_{a} (kJ mol^{-1})	ΔH^{o}_{a} (kJ mol^{-1})	ΔS^{o}_{a} (J mol^{-1})
0	19.9	16.6	-271.0
5	22.4	19.1	-269.6
10	27.4	24.1	-256.0
20	28.3	24.9	-256.0
40	30.8	27.5	-250.0
60	33.3	30.8	-241.7

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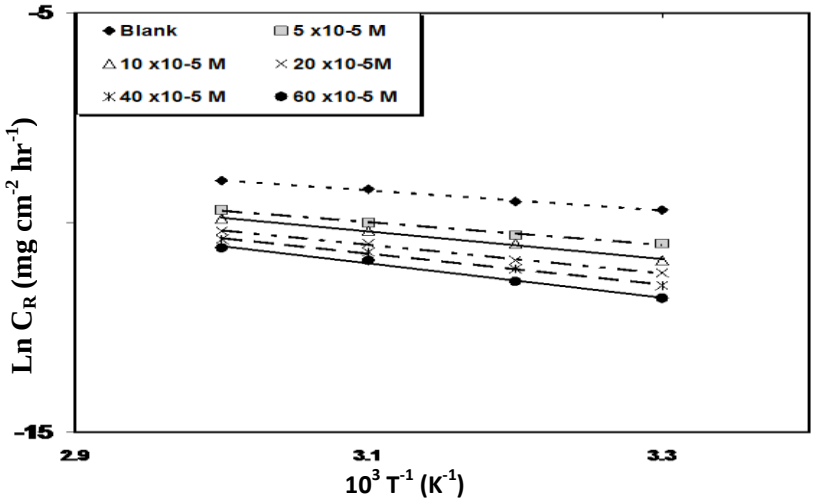

Fig.5. Arrhenius plots for carbon steel in 1.0 M HCl solution with different concentrations of the inhibitor.

Generally, the higher values of activation energy (E^{o}_{a}) in the presence of inhibitor than in its absence is attributed to its physical adsorption, while the chemisorption is pronounced in the opposite case [28,29].In the present study, the apparent activation energy increased with increasing concentrations of inhibitor. This increase in the apparent activation energy may be understood as physical adsorption [30]. Szauer and Brand [28] explained that the increase in activation energy can be ascribed to significant decrease in the adsorption of the inhibitor molecules on the carbon steel surface with increase in temperature. A relevant increase in corrosion rates occurs due to the exposure of greater metallic area to the acid environment.

An alternative form of Arrhenius equation is the transition state equation [27]:

$$C_R = RT/Nh \exp(\Delta S^{o}_{a}/R) \exp(-\Delta H^{o}_{a}/RT) \qquad (8)$$

Where, h is Plank's constant, N is Avogadro's number, ΔS°_{a} is the entropy of activation, and ΔH^{o}_{a} is the enthalpy of activation. A plot of log (C_R/T) versus 1/T gives a straight line as shown in Fig.6 with a slope of ($-\Delta H^{o}_{a}$/2.303R) and an intercept of [log(R/Nh) + (ΔS^{o}_{a}/R)], from which the values of ΔH^{o}_{a} and ΔS^{o}_{a} were calculated and listed in Table 3.

Inspection of these data reveals that the thermodynamic parameters (ΔH^{o}_{a} and ΔS°_{a}) of dissolution reaction of carbon steel in 1.0 M HCl in the presence of drug inhibitor are higher than those in its absence. The positive sign of enthalpies reflect the endothermic nature of steel dissolution process meaning that dissolution of steel is difficult [31].

On comparing the values of the entropy of activation ΔS^{o}_{a} given in Table 3, it is clear that entropy of activation increased positively in the presence of drug inhibitor. The increase of ΔS^{o}_{a} reveals that an increase in disordering takes place on going from reactant to the activated complex [32].

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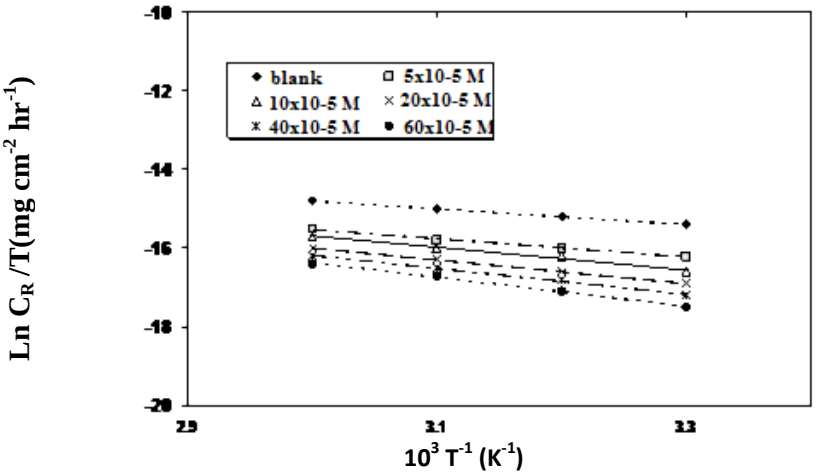

Fig. 6. Transition state plots for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of the inhibitor

Potentiodynamic polarization measurements

The effect of different concentrations of the inhibitor on the mechanism of inhibition can be investigated from the polarization curve measurements Fig.7 shows the anodic and cathodic polarization curves measured in 1.0 M HCl with different concentrations of the inhibitor. It can be easily noticed from the polarization curves that whilst the inhibitor primarily reduces the anodic, metal dissolution reaction it appears to affect the rate and mechanism of the cathodic reaction. It is illustrated that Tafel lines shifted towards more negative and more positive potentials during the anodic and cathodic processes respectively, relative to the blank curve. This means that the selected compound acts as mixed-type inhibitor.

The electrochemical parameters including corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) determined from the polarization curves are presented in Table 4**.** The Table also reports the percentage efficiency (η %) and degree of surface coverage (θ) determined from the corrosion current density, I_{corr}, using the relationships:

$$\eta\ \% = (I^o - I)/I^o \times 100 \quad (9)$$

$$\theta = I^o - I/I^o \quad (10)$$

where, I^o and I are the corrosion current densities in the absence and presence of inhibitor, respectively. As reflected from the data of Table 4 that the addition of drug inhibitor decreases corrosion current density. Furthermore, the degree of surface coverage and the percentage efficiency increases with increasing the inhibitor concentration. Also, it can be clearly seen that corrosion potential (E_{corr}) is shifted to the noble direction, this behavior shows that the drug inhibitor acts as a good inhibitor for the corrosion of carbon steel in HCl media.

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Table 4 Corrosion parameters obtained from polarization measurements for carbon steel in 1.0 M HCl containing various concentrations of inhibitor at room temperature.

Conc. ($Mx10^{-5}$)	$E_{corr.}$ (mV)	$I_{corr.}$, (m A cm^{-2})	b_a, (mV)	b_c, (mV)	(θ)	η %
0	-544	3.59	316	-351	-	-
5	-519	0.14	81.7	-133	0.96	96.0
10	-508	0.10	68.8	-134	0.972	97.2
20	-509	0.07	83.9	-141	0.98	98.0
40	-522	0.05	118	-143	0.985	98.5
60	-524	0.04	129	-145	0.99	99.0

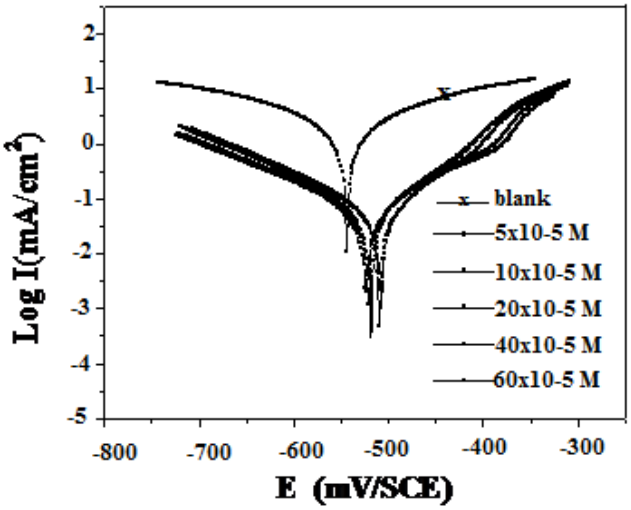

Fig 7. Polarization curves for carbon steel in 1.0 M HCl in absence and presence of different concentrations of drug inhibitor.

Electrochemical Impedance Spectroscopic measurements (EIS)

A better understanding of the corrosion mechanism taking place at the electrode surface was attained through EIS measurements. The impedance measurements were carried out under Potentiostatic conditions after immersion for 30 min in 1.0 M HCl and in the presence of the studied compound. Fig.8a shows the Nyquist plots for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of drug inhibitor. All experimental spectra have a depressed semicircular shape in the complex impedance plane, with the center under the real axis.

It is essential to develop the appropriate models for the impedance which can then be used to fit the experimental data and extract the parameters which characterize the corrosion process.

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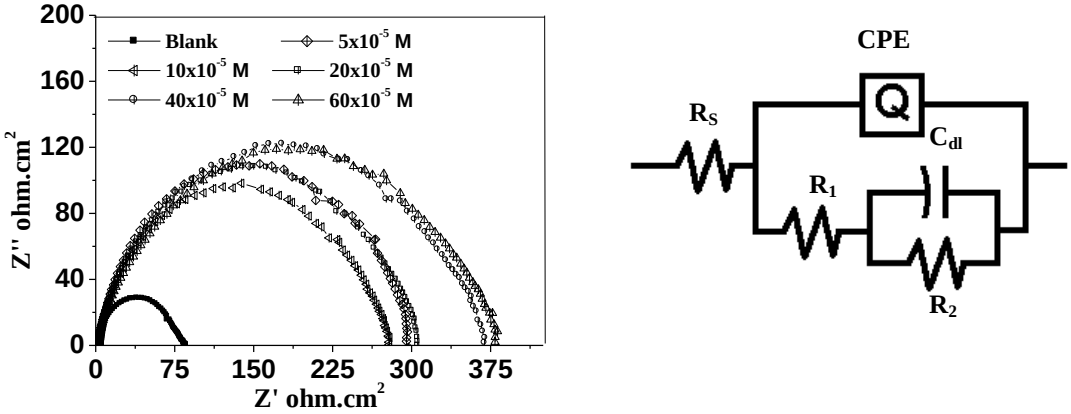

Fig. 8. Nyquist plot, together with the equivalent circuit used to simulate the impedance data, recorded for carbon steel in 1.0 M HCl solution in absence and presence of different concentrations of drug inhibitor.

Electrically equivalent circuits are generally used to model the electrochemical behavior and to calculate the parameters of interest, such as electrolyte resistance (R_s), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) [33].The equivalent circuit model used to fit the experimental data is shown in Fig.8b. When a non-ideal frequency response is present, it is commonly accepted to use distributed circuit elements in an equivalent circuit. It is worth mentioning that the double layer capacitance (C_{dl}) value is affected by imperfections of the surface, and that this effect is simulated via a constant phase element (CPE) [34].

The constant phase element (CPE) has a non-integer power dependence on the frequency and is used to explain the depression of the capacitance semi-circle, which corresponds to surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [35,36], etc. The CPE impedance (Z_{CPE}) is obtained by the following equation:

$$Z_{CPE} = Q^{-1} (j\omega)^{-n} \qquad (11)$$

Where, *Q* is the CPE coefficient, *n* the CPE exponent (phase shift), ω the angular frequency (ω = 2πf, where *f* is the AC frequency), and j here is the imaginary unit. When the value of n is 1, the CPE behaves like an ideal double-layer capacitance (C_{dl}) [35, 37]. The correction of capacity to its real values is calculated from:

$$C_{dl} = Q (\omega_{max})^{n-1} \qquad (12)$$

Where, ω_{max} is the frequency at which the imaginary part of impedance (−Z") has a maximum [38].The calculated structure parameters are presented in Table 5.

Data in Table 5 reveals that R_{ct} value increase with increasing drug inhibitor concentration and while, C_{dl} value decreases much in the presence of inhibitor. This situation was a result of the adsorption of inhibitor molecules at the metal/solution interface. A decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer can cause decrease in C_{dl} values, suggesting that the inhibitor molecules with low dielectric constant replace the water molecules with high dielectric constant.

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Table 5 Electrochemical impedance parameters and inhibition efficiency for corrosion of carbon steel in 1.0 M HCl in the presence and absence of different concentrations of drug inhibitor.

Conc. ($Mx10^{-5}$)	R_s ($\Omega\ cm^2$)	Q(CPE) ($\Omega^{-1}\ cm^{-2}$)	n	R_p ($\Omega\ cm^2$)	C_{dl} ($\mu F\ cm^{-2}$)	R_{ct} (Ωcm^2)
0	22.5	9.0×10^{-5}	0.69	40	3.00×10^{-4}	87
5	2.85	2.9×10^{-5}	0.90	54	8.32×10^{-6}	235
10	2.00	2.25×10^{-5}	0.92	105	8.06×10^{-6}	278
20	2.00	1.30×10^{-5}	0.94	108	8.00×10^{-6}	306
40	2.01	1.25×10^{-5}	0.95	140	7.90×10^{-6}	323
60	2.16	9.50×10^{-6}	0.96	184	2.02×10^{-6}	374

Surface Study

X- ray diffraction analysis

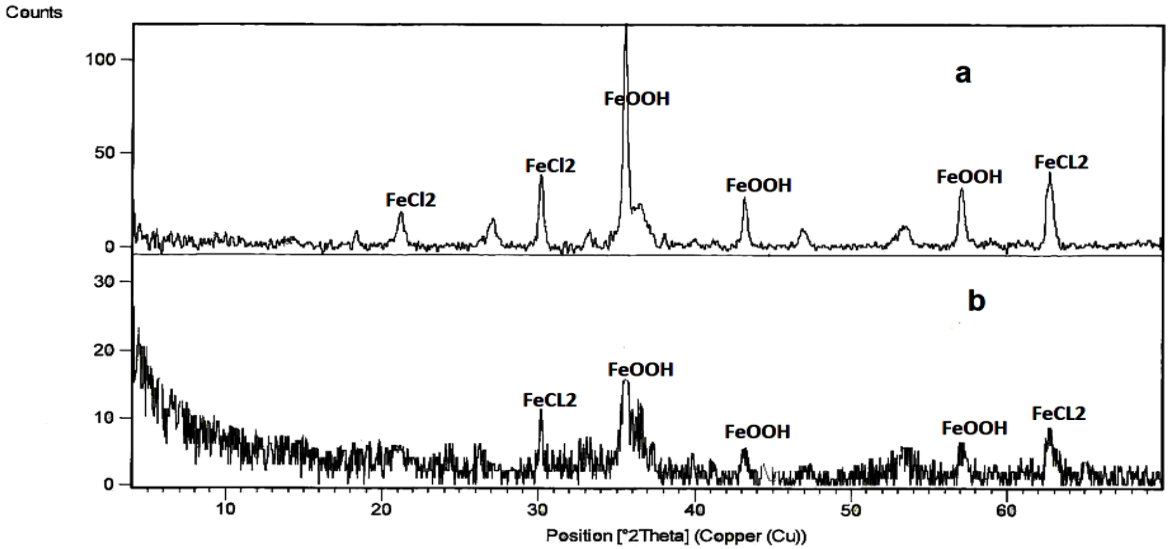

Fig.9- XRD patterns of corrosion products formed on the surface of carbon steel, (a) After 48 h immersion in 1.0 M HCl, (b) After immersion in 1.0 HCl containing 60x 10^{-5} M inhibitor.

Compositional analysis of the corrosion products films formed on the surface of carbon steel coupons immersed in 1.0 M HCl in the absence and presence of optimum concentration of the studied inhibitor (60 x 10^{-5} M) were performed using X-ray diffraction and the recorded diffraction patterns are presented in Fig.9 (a,b) respectively. In the absence of inhibitor, the XRD pattern (Fig.9a) revealed the presence of a large proportion of goethite (α-FeOOH) as indicated from its characteristics peaks at 2θ equal (35.2,43.5 and 56.2). Goethite is the expected phase as corrosion product in the case of carbon steel in chloride environments [39], the pattern also shows small amount of $FeCl_2$ at 2θ equal (21.2.30.2 and 62.6) . The XRD pattern of inhibited surface (Fig.9b) shows the same two main phases observed previously but the intensity of the peaks becomes extremely weak compared to those detected in the absence of inhibitor. The X-ray diffraction (XRD) analysis can be used not only for identification of crystalline phases in corrosion products but also for their quantitative phase analysis based on measuring the intensity of a single diffraction line or even all the lines in the pattern [40]. It can be noted from the comparative patterns shown in Fig.9 (a, b) that addition of the optimum concentration of the

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studied inhibitor leads to a noticeable decrease in the height of the characteristic peaks of both goethite and $FeCl_2$. As the height of the phase peak correlates with its concentration in the sample [41], so the decrease in the height of the corrosion product phase observed in (Fig.9b) can be considered as a semi-quantitative indication for the suppression of the corrosion process and hence gives good evidence for the excellent inhibitive effect of the studied drug inhibitor for carbon steel corrosion in acidic media. However, the inhibitor surface film was not detected in the X-ray pattern, possibly because of the poor crystallinity of the material, and may be a due to the fact that the film is very thin.

EDX examination of the electrode surface

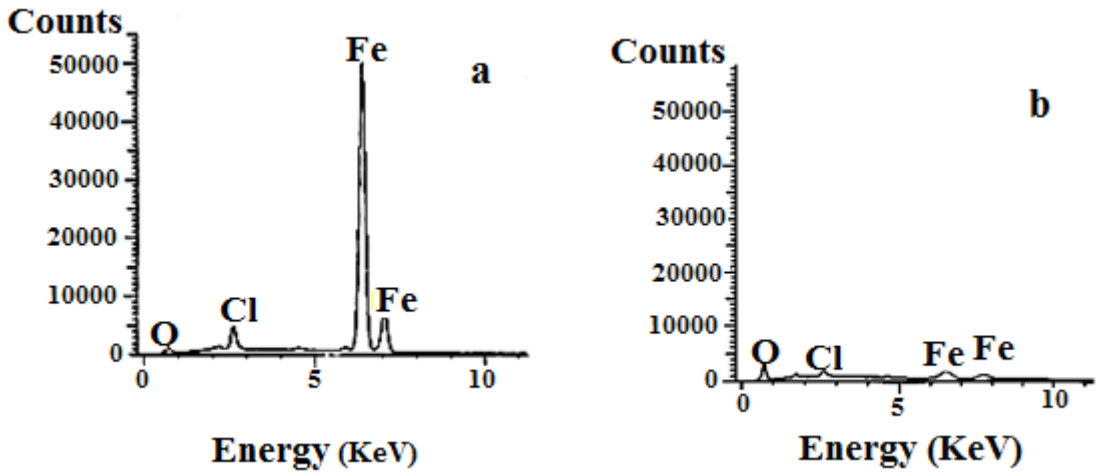

Fig. 10. EDX spectra of carbon steel specimens, (a) After 48 h of immersion in 1.0 M HCl and (b) After 48 h of immersion in 1.0 M HCl containing 60x 10^{-5} M inhibitor

Energy dispersive X-ray analysis (EDXA) technique was employed in order to get additional information on the inhibition mechanism. Fig.10 (a, b) presents an EDX panorama recorded for carbon steel samples exposed 48 h in 1.0 M HCl solution in the absence and presence of optimum concentration of Cefazolin .The EDX spectra of uninhibited surface Fig.10 a clearly indicates the presence of Fe signal, the major constituent element in carbon steel sample, small Cl and O signals in the weight percentage of 93.57%, 5.04%, 1.93% respectively. Fig.10 b representing the EDX spectra of inhibited surface clearly shows suppression of Fe, Cl and O lines. This observation confirmed that addition of drug inhibitor to the tested solution resulted in formation of adsorbed layer of inhibitor on the metal surface and hence suppressed the corrosion process. Therefore, EDX and XRD examinations of the electrode surface support the results obtained from the electrochemical methods that the studied drug inhibitor is a good inhibitor for carbon steel in HCl solution.

Mechanism of inhibition

In HCl solution the following mechanism is proposed for the corrosion of iron and steel [42]. According to this mechanism anodic dissolution of iron follows:

$$Fe + Cl^- \leftrightarrow (FeCl^-)_{ads} \quad (13)$$

$$(FeCl^-)_{ads} \leftrightarrow (FeCl)_{ads} + e^- \quad (14)$$

$$(FeCl)_{ads} \rightarrow (FeCl^+)_{ads} + e^- \quad (15)$$

$$FeCl^+ \leftrightarrow Fe^{2+} + Cl^- \quad (16)$$

The cathodic hydrogen evolution follows:

$$Fe + H^+ \leftrightarrow (FeH^+) \quad (17)$$

$$(FeH^+)_{ads} + e^- \rightarrow (FeH)_{ads} \quad (18)$$

$$(FeH^+)_{ads} + H + e^- \rightarrow Fe + H_2 \quad (19)$$

The inhibition efficiency of the examined drug against the corrosion of carbon steel in 1 M HCl can be explained on the basis of the number of adsorption sites, molecular size and mode of interaction with the metal surface [43]. Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution; the presence of a metal having vacant low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatoms with lone pair electrons. However, the compound reported is an organic base which can be protonated in an acid medium. Thus they become cations, existing in equilibrium with the corresponding molecular form as the following:

$$CFZ + xH \leftrightarrow [CFZ_x]^{x+} \quad (20)$$

The protonated compound, however, could be attached to the carbon steel surface by means of electrostatic interaction between Cl^- and protonated cefazolin since the carbon steel surface has positive charge in the HCl medium [44]. This could be further explained based on the assumption that in the chloride media, the negatively charged Cl^- would attach to positively charged surface. When cefazolin adsorbs on the carbon steel surface, electrostatic interaction takes place by partial transference of electrons from the polar atom (N atom and delocalized π-electrons of the aromatic ring) of the studied inhibitor to the metal surface. In the present study, the value of ΔG^o_{ads} is -37.1 kJ mol^{-1} indicating that, adsorption of the examined drug inhibitor on the surface of carbon steel involves both physical and chemical processes.

CONCLUSION

1) The studied pharmaceutically active compound acts as efficient inhibitor for the corrosion of carbon steel in 1.0 M HCl.
2) The inhibition efficiency of the studied drug inhibitor increases by increasing the inhibitor concentration but decreases with temperature.
3) The adsorption of the studied drug inhibitor obeys Langmuir adsorption isotherm and involves both physical and chemical processes.
4) The adsorption process is a spontaneous and exothermic process accompanied by an increase of entropy.
5) XRD and EDX studies confirmed the excellent inhibition efficiency of the studied drug inhibitor.

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