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Research Article

Corrosion Inhibition and Adsorption Properties of Cefixime on Carbon Steel in Acidic Medium

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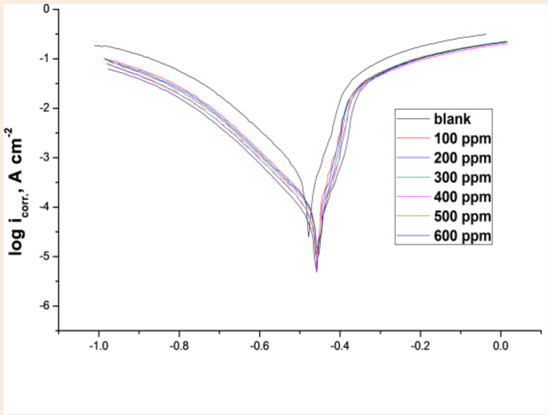
Abstract

The corrosion inhibition of carbon steel in H_2SO_4 in the presence of cefixime was studied using weight loss, potentiodynamic polarization, electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS) techniques. The study revealed that the corrosion rate increases with temperature. Addition of cefixime to the corrodent solution lowered the corrosion rate of carbon steel. Inhibition efficiency (%IE) of cefixime was found to increase with concentration and decreased with temperature. Adsorption of cefixime molecule on carbon steel surface was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.

Keywords: Cefixime, corrosion inhibition, carbon steel, adsorption



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Introduction

A number of heterocyclic compounds containing N, O and S either in the aromatic or long chain carbon system have been reported to be effective inhibitors [1-4]. These inhibitors have extended π-electron systems and functional groups (such as -C=C-, -OR, -OH, -NR2, -NH2 and –SR). The functional groups provide electrons that facilitate the adsorption of the inhibitor on the metal surface [5-10]. Some drugs (such as ampicillin, ampiclox, cloxacillin, tetracycline, methocarbamol, orphenadrine, penicillin G, azithromycin, etc) have been found to be good inhibitors for the corrosion of metals. Many authors generally agree that drugs are inhibitors that can compete favorably with green corrosion inhibitors and that most drugs can be synthesized from natural products. The choice of some drugs used as corrosion inhibitors is based on the following: (a) drug molecules contain oxygen, nitrogen and sulphur as active centers, (b) drugs are reportedly environmentally friendly and important in biological reactions and (c) drugs can be easily produced and purified [11-15].

Dithiobiurets exhibited the best performance towards the corrosion of carbon steel in H_2SO_4 solutions and showed much less toxicity [16–19]. The inhibition action of these drugs was attributed to blocking the surface via formation of insoluble complexes on the metal surface. Cefixime is effective in a large variety of bacterial infections, such as respiratory tract, ear, skin, gonorrhea, otitis media, and urinary tract infections. A detailed literature review shows no data are available regarding the behavior of cefixime as inhibitor for protection of carbon steel against corrosion.
In the present study, the inhibitive properties of this compound are reported for the first time, using chemical and electrochemical techniques. The inhibition mechanism has been discussed on the basis of these studies.

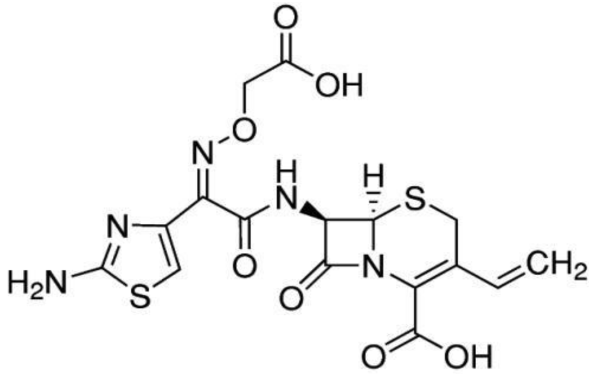
Experimental procedure

Weight loss method

Materials used for the study were carbon steel sheet of composition (weight %) Mn (0.03), P (0.033), C (0.2), Si (0.14) and Fe balance. The sheet was mechanically pressed cut to form different coupons, each of dimension, 2 x 2 x 0.1 cm. Each coupon was degreased by washing with ethanol, rinsed in acetone, allowed to dry and preserved in a desiccator. All reagents used for the study were Analar grade and double distilled water was used for their preparation. Concentration of H_2SO_4 used for the study was 1 N while those of cefixime (the inhibitor used) were 200-600 ppm.

All the experiments were performed at room temperature for an immersion time of 3 hrs. The inhibition efficiency (% IE) and degree of surface coverage (θ) were calculated from the equation (1) [21] where, W_O and W are the weight losses without and with inhibitor, respectively

$$\% IE = \theta \times 100 = [(W_O - W)/ W_O] \times 100 \qquad (1)$$



Scheme 1 Molecular structure of cefixime; the molecular formula of Cefixime is $C_{16}H_{15}N_5O_7S_2$ and its molecular weight is 453.4

The electrochemical studies were made using a three electrode cell assembly at room temperature [22, 23]. The working electrode was a carbon steel of the above composition of 1 cm^2 area and the rest being covered by using commercially available lacquer. A rectangular platinum foil of 1 cm^2 was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The working electrode was abraded with different grades of emery papers (up to1200 grit size), washed with double distilled water and degreased with acetone. The polarization study was carried out from -1.0 to 0.0 V versus SCE with scan rate of 1 mV/s. The inhibition efficiency has been calculated using the relationship:

$$\% IE = \theta \times 100 = [(i_{corr} - i_{corr(inh))} / i_{corr}] \times 100 \qquad (2)$$

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

The electrochemical impedance spectroscopy (EIS), spectra were recorded at open circuit potential (OCP) after immersion the electrode for 30 min in the test solution. The signal was 5 mV peak to peak and the frequency range studied was between 100 kHz and 0.2 Hz. The inhibition efficiency (% IE) and the surface coverage (θ) of the inhibitor obtained from the impedance measurements were calculated by applying the following relations:

$$\% IE = \Theta \times 100 = [1- (R^o_{ct} / R_{ct})] \times 100 \qquad (3)$$

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

For the electrochemical frequency modulation technique (EFM), a potential perturbation by two sine waves of different frequencies is applied to the system. As a corrosion process is nonlinear in nature, responses are generated at more frequencies than the frequencies of the applied signal. The current responses can be measured at zero, harmonic, and intermodulation frequencies. Analysis of these current responses can result in the corrosion current density and Tafel parameters. The inhibition efficiency (%IE) and the surface coverage (θ) of the inhibitor obtained from eq. (2) All Electrochemical experiments were carried out using Potentiostat/Galvanostat/ Zra analyzer (Gamry PCI 300/4). A personal computer with EIS300 software for EIS, DC105 software for polarization and EFM140 software for EFM measurements and E_{chem} Analyst 5.21 was used for data fitting and calculating.

Results and discussion

Weight loss measurements

Figure 1 represents the weight loss-time curves in the absence and presence of different concentrations of cefixime. **Table 1** collects the values of surface coverage, inhibition efficiency and corrosion rate obtained from weight loss measurements in 1 N H_2SO_4 at 25°C. The results of this Table show that the presence of cefixime reduces the corrosion rate of C- steel in H_2SO_4 and hence, increase the inhibition efficiency.

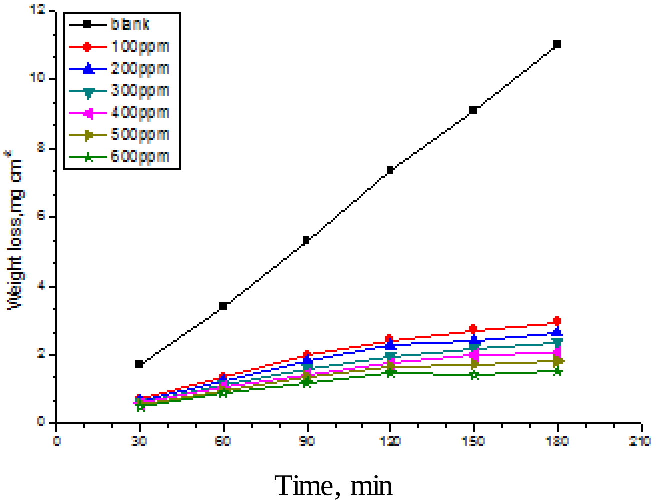


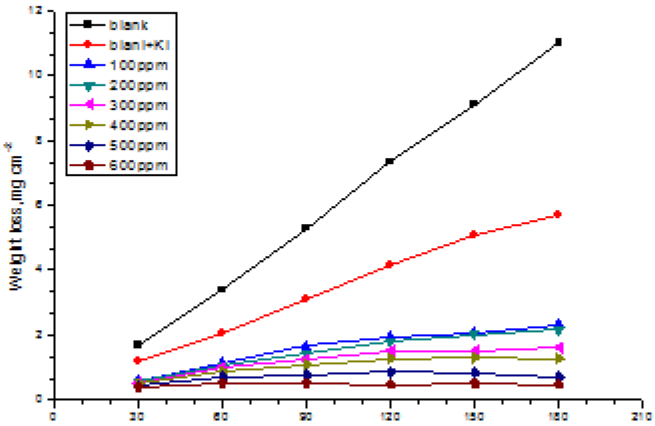
Figure 1 Weight loss-time curves for C-steel dissolution in 1N H_2SO_4 in the absence and presence of different concentrations of cefixime at 25°C

Table 1 Inhibition efficiency (% IE) and corrosion rate (CR) at different concentrations of cefixime for carbon steel in 1 N H_2SO_4 as determined by weight loss method after 90 min immersion at 25ºC

[Inhibitor] ppm	Inhibition efficiency (%IE)	CR x 10^{-3} (mg $cm^{-2}min^{-1}$)
100	62.30	22
200	65.40	20
300	69.50	18
400	72.90	16
500	74.40	15
600	77.70	13

Role of KI in corrosion-inhibition of C- steel in H_2SO_4 solutions and its synergistic effect

The effect of addition of KI on the corrosion of C- steel in 1 N H_2SO_4 solution in the absence and presence of different concentrations of cefixime was studied by weight loss method. **Figure 2** shows the weight loss-time curves for C- steel in 1 N H_2SO_4 solution in the absence and presence of different concentrations of cefixime in addition to the presence of 0.01M of KI. The values of inhibition efficiency (%IE) corrosion rate (CR) and S_Θ (synergism parameter) were shown in the **Table 2**.



Time, min.

Figure 2 Weight loss-time curves for C-steel dissolution in 1 N $H_2SO_4$and 0.01M KI in absence and presence of different concentrations of cefixime at 25°C

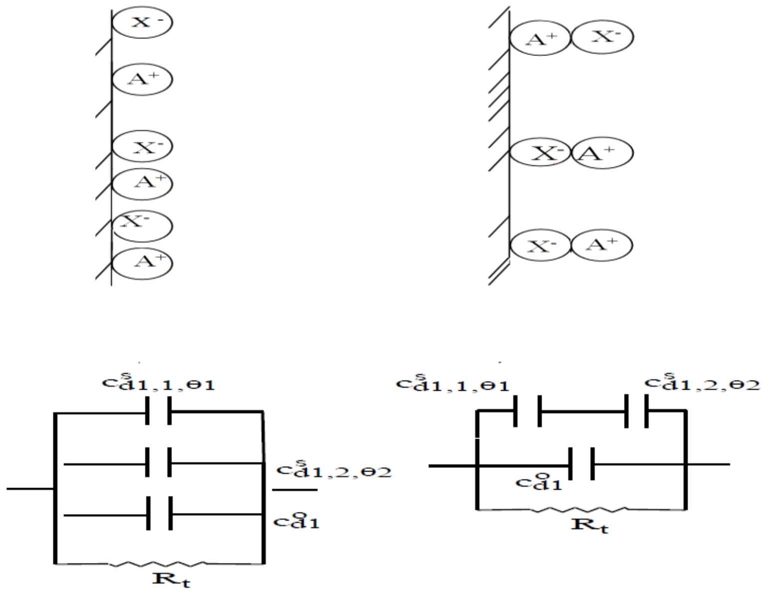
Table 2 Inhibition efficiency (% IE) ,corrosion rate(CR)and synergistic parameter (S_Θ) at different concentrations of cefixime for carbon steel in 1 N H_2SO_4 and in presence of 0.01M KI as determined by weight loss method after 90 min immersion at 25°C

[Inhibitor], ppm	Inhibition efficiency (% IE)	CR x 10^{-3} (mg $cm^{-2}min^{-1}$)	S_Θ
100	68.6	18	1.070
200	72.8	16	1.074
300	76.8	14	1.076
400	79.5	12	1.077
500	85.4	9	1.022
600	90.4	6	1.354

The synergism parameter (S_θ) were calculated using the relationship given by Aranmki and Hackerman [24].

$$S_\Theta = (1 - \theta_{1+2}) / (1 - \theta'_{1+2}) \qquad (4)$$

Where, $\theta_{1+2} = (\theta 1 + \theta 2) - (\theta 1\ \theta 2)$, θ_1= surface coverage by anion, θ_2= surface coverage by cation, θ'_{1+2}= measured surface coverage by anion and cation. This equation actually compares the corrosion rate of either anion or cation and of the inhibitor mixture (anion + cation). If anions and cations have no effect on each other and adsorbed at metal surface independently, the S_Θ value should be equal 1. Furthermore, synergistic effects are observed if $S_\Theta > 1$ and activation of corrosion is observed if $S_\Theta < 1$. It can be seen from Table (2) that the addition of KI inhibits the corrosion of carbon steel to a large extent. This can be interpreted according to Schmitt and Bedbur [25], which proposed two types of joint adsorption namely competitive and cooperative. In competitive adsorption the anions and cations are adsorbed at different sites on the electrodes surface, and in cooperative adsorption, the anions are chemisorbed on the surface and the cations are adsorbed on a layer of the anions, a part from the adsorption on the surface directly. These two types are illustrated in **Figure 3** [26].



Competitive adsorption Cooperative adsorption

Figure 3 Types of joint adsorption (competitive and cooperative)

Potentiodynamic polarization measurements

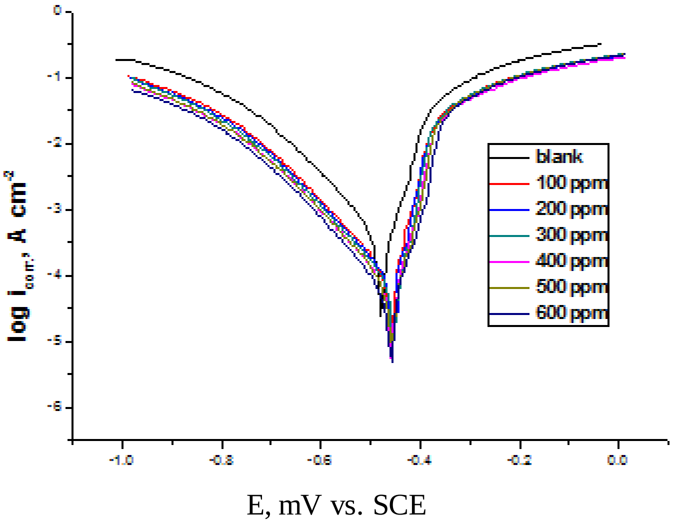


Figure 4 Potentiodynamic polarization curves for the dissolution of carbon steel in 1 N H_2SO_4 in the absence and presence of different concentrations of compound cefixime at 25ºC

Figure 4 shows the potentiodynamic polarization curves for C- steel without and with different concentrations of cefixime at 25ºC. The obtained electrochemical parameters; cathodic (β_c) and anodic (β_a) Tafel slopes, corrosion potential (E_{corr}), corrosion current density (i_{corr}), and polarization resistance (R_p) were obtained and are listed in **Table 3**. **Table 3** shows that i_{corr} decreases by adding cefixime and by increasing its concentration. In addition, E_{corr} does not change obviously. Also, β_a and β_c do not change markedly, which indicates that the mechanism of the corrosion reaction of C-steel does not change. Figure (4) clearly shows that both anodic and cathodic reactions are inhibited, which indicates that investigated cefixime acts as mixed-type inhibitor [27-28]. The inhibition achieved by this compound.

Table 3 The effect of concentrations of investigated compound on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_c, β_a), corrosion rate (CR), inhibition efficiency (% IE) and degree of surface coverage (θ) of carbon steel in 1 N H_2SO_4 at 25ºC

Comp.	[Inh.] ppm	$-E_{corr}$ mV vs SCE	$i_{corr.}$ $\mu A\ cm^{-2}$	β_c $mV\ dec^{-1}$	β_a $mV\ dec^{-1}$	$R_p \times 10^{-2}$ $\Omega\ cm^2$	CR mmy^{-1}	θ	% IE
blank	0.0	487	896.1	221	180	47.99	10.402	----	----
cefixime	100	460	258.6	189	145	137.8	3.002	0.711	71.1
	200	455	205.5	185	141	169.0	2.385	0.771	77.1
	300	455	186.3	183	139	183.9	2.162	0.792	79.2
	400	458	162.4	182	140	211.7	1.885	0.819	81.9
	500	458	151.1	179	137	223.0	1.753	0.831	83.1
	600	460	118.2	177	134	279.8	1.373	0.868	86.8

Adsorption isotherms

One of the most convenient ways of expressing adsorption quantitatively is by deriving the adsorption isotherm that characterizes the metal/inhibitor/ environment system [29]. The surface coverage (θ) values were tested graphically to allow fitting of a suitable adsorption isotherm. The plot of θ/ (1- θ) versus C yielded a straight line at 25ºC (Fig. 5), this proving that the adsorption of cefixime on C-steel surface obeys Langmuir adsorption isotherm according to the following equation:

$$\theta / (1-\theta) = K_{ads}C \qquad (5)$$

Where, K_{ads} is equilibrium constant of adsorption process and Cis the cefixime concentration.

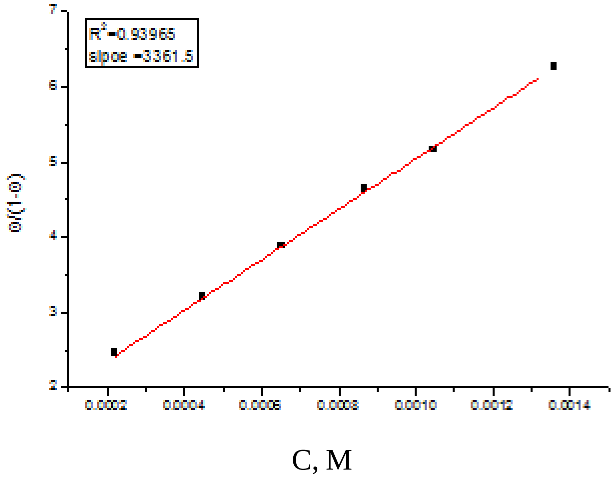


Figure 5 Langmuir adsorption isotherm plotted as ϴ/1-ϴ vs C curves for C-steel in 1 N H_2SO_4 solutions at 25ºC from potentiodynamic data

K_{ads} is related to the standard free energy of adsorption ΔG°_{ads} by equation (6) [30]:

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

The value of 55.5 is the concentration of water in solution expressed in mole per liter. The calculated ΔG°_{ads} values were also given in Table (4).Inspection of the data of this Table shows that large value of ΔG°_{ads} and its negative sign, indicate that the adsorption of cefixime on C-steel surface is proceeding spontaneously and accompanied by highly – efficient adsorption.

The enthalpy of adsorption (ΔH°_{ads}) can also be calculated from the Gibbs–Helmholtz equation [31]:

$$(\Delta G^{\circ}_{ads} / T) = (\Delta H^{\circ}_{ads}/T) + \text{constant} \qquad (7)$$

The variation of (ΔG°_{ads} / T) with 1/T gives a straight line with a slope which is equal to ΔH°_{ads} (Fig. 6). It can be seen from the figure that (ΔG°_{ads} / T) decreases with 1/T in a linear fashion. The enthalpy and entropy for the adsorption of cefixime on carbon steel were also deduced from the thermodynamic basic equation [32]:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{o}_{ads} \qquad (8)$$

Where, ΔS^{o}_{ads} is the entropy changes of adsorption process. A plot of ΔG°_{ads} versus T was linear (Fig. 6) with slope equals to ΔS^{o}_{ads} and intercept equals ΔH°_{ads}. The enthalpy of adsorption ΔH°_{ads} and the entropy of adsorption ΔS^{o}_{ads} obtained are negative. The negative sign of ΔH°_{ads} indicates that the adsorption of cefixime is an exothermic process. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of ΔH°_{ads}. For physisorption process, the enthalpy of adsorption is lower than 40 kJ mol^{-1} while that for chemisorption approaches100 kJ mol^{-1}[33]. In the present study, the absolute value of enthalpy of adsorption obtained is typical of physisorption. Values of ΔH°_{ads} obtained by the two methods are in good agreement. The entropy of adsorption was negative because inhibitor molecule freely moving in the bulk solution (inhibitor molecule were chaotic), were adsorbed in an orderly fashion onto the carbon steel, resulting in a decrease in entropy [30]. Moreover, from thermodynamic principles, since the adsorption was an exothermic process, it must be accompanied by a decrease in entropy

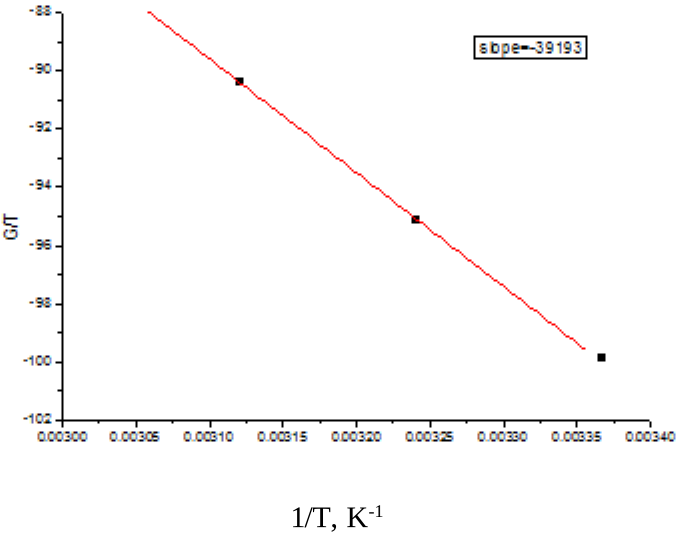


Figure 6 $\Delta G^{o}/T$ versus 1/T curves for cefixime

Table 4 Equilibrium constant of adsorption reaction (K_{ads}), free energy of adsorption(ΔG°_{ads}), enthalpy of adsorption(ΔH°_{ads}) and entropy of adsorption(ΔS^{o}_{ads})of cefixime on C-steel surface in 1 N H_2SO_4 at different temperatures

Temperature	K M^{-1}	$-\Delta G^{\circ}_{ads}$ kJ mol^{-1}	$-\Delta H^{\circ}_{ads}$ kJ mol^{-1}	$-\Delta S^{o}_{ads}$ J $mol^{-1}K^{-1}$
25	3297.42	30.0	39.2	30.6
35	1519.69	29.1		32.9
45	810.42	28.3		34.1
55	856.80	29.4		30.0

Effect of temperature

To investigate the mechanism of inhibition and to determine the activation energy of corrosion process from potentiodynamic polarization of C- steel in 1 N H_2SO_4 were studied at various temperatures (25–55C°) in the absence and presence of different concentrations of cefixime. This inhibitor was found to retard the corrosion process at lower temperatures [35] whereas the inhibition are considerably decreased at elevated temperatures. The increasing of the corrosion rate with increasing the temperature is suggestive of physical adsorption of the investigated inhibitor on C-steel surface.

The obtained electrochemical parameters; cathodic (β_c) and anodic (β_a) Tafel slopes, corrosion potential (E_{corr}), corrosion current density (i_{corr}), and polarization resistance (R_p) were obtained and are listed in Table (5).Table (5) shows that i_{corr} increases by by increasing temperature. Figure (7) represents the Arrhenius plots of natural logarithm of corrosion rate (k) versus 1/T, for C- steel in 1 N H_2SO_4 solutions, in absent and presence of different concentration of cefixime. The values of slopes of these straight lines permit the calculation of the activation energy according to:

$$k = A \exp (- E_a^*/ RT) \qquad (9)$$

where, k is the corrosion rate, A is the pre-exponential factor and E_a^* is the apparent activation energy. The values of E_a^* are given in **Table (6)**. The results of Table (8) revealed that, the values of E_a^* were increased by increasing the concentration of the investigated cefixime indicating the dissolution of C-steel under these conditions is activation controlled and also, indicates the energy barrier of the corrosion reaction increases in the presence of these additives. Similar results were obtained by other authors [36-38]. The higher values of E_a^* are good evidence for the strong adsorption of cefixime on C-steel surface.

An alternative formulation of Arrhenius equation is the transition state equation [39]:

$$k = RT/ Nh + \Delta S^*/ 2.303R + (-\Delta H^*/ 2.303RT \qquad (10)$$

By blotting log k/T against 1/ T we obtain the enthalpy change ($\Delta H^{*)}$ and entropy change (ΔS^*) from the slopes and intercepts, respectively.

The values of (ΔH^*) are positive and higher in the presence of the cefixime than in its absence. This implies that energy barrier of the corrosion reaction in the presence of the investigated cefixime increases and indicates the endothermic behavior of the corrosion process. On the other hand ΔS^* values are lower and have negative values in presence of the additives, this means that addition of cefixime cause a decrease in the disordering in going from reactants to the activated complexes [40, 41].

Table 5 The effect of concentrations of investigated cefixime on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_c, βa), corrosion rate (CR), inhibition efficiency (% IE) and degree of surface coverage (θ) of carbon steel alloy in 1N H_2SO_4 at 25ºC

Comp	[Inh] ppm	$-E_{corr}$ mV	$i_{corr.}$ µA cm^{-2}	β_c mV dec^{-1}	β_a mV dec-^{1}	R_px 10^{-2} Ω cm^2	CR mmy^{-1}	θ	% IE
blank	0.0	489	2543	284	227	21.52	29.52	------	------
cefixime	100	478	1991	262	198	24.63	23.11	0.217	21.7
	200	489	1889	244	196	24.99	21.93	0.257	25.7
	300	474	1694	253	211	29.47	19.67	0.334	33.4
	400	483	1577	239	193	29.41	18.30	0.380	38.0
	500	488	1338	244	196	35.25	15.53	0.474	47.4
	600	483	1171	236	183	38.16	13.59	0.540	54.0

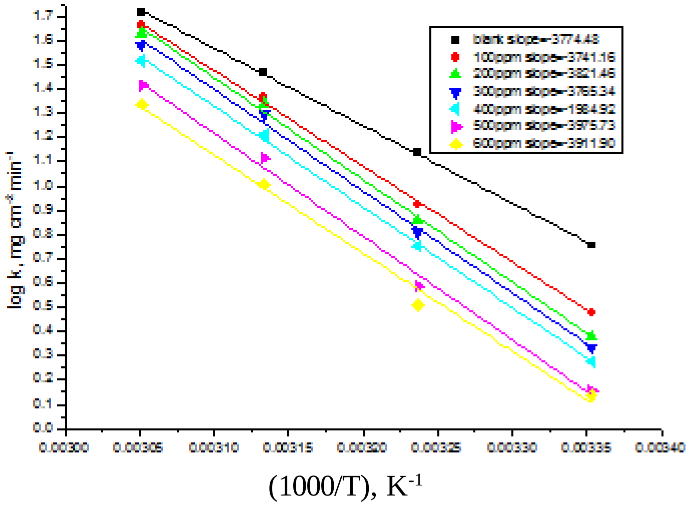


Figure 7 Arrhenius plots log i_{corr} vs 1/ T for corrosion of carbon steel in1 N H_2SO_4 in the absence and presence of cefixime

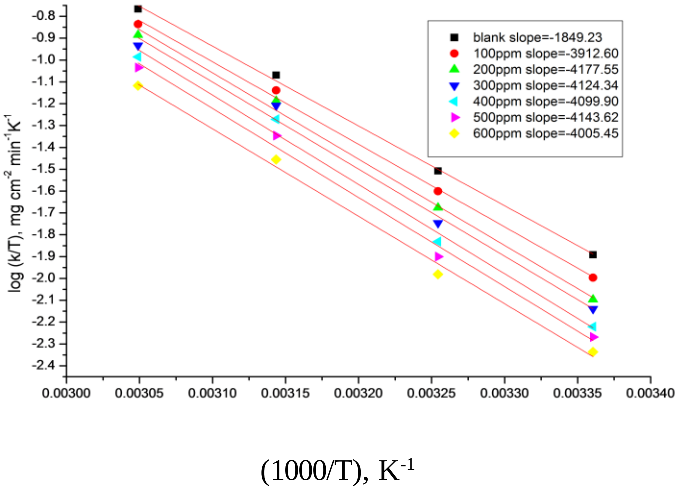


Figure 8 Transition state plots of log i_{corr} / T vs 1/ T for corrosion of carbon steel in1 N H_2SO_4 in the absence and presence of investigated cefixime

Table 6 Thermodynamic activation parameters for the dissolution of carbon steel in 1 N H_2SO_4 in the absence and presence of different concentrations of cefixime

inhibitor	Conc. M	E^*_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}
blank	0.0	38.0	35.4	106.6
cefixime	0.00022	77.5	74.9	14.4
	0.00044	82.6	80.0	29.9
	0.00066	81.6	69.7	25.9
	0.00088	81.1	78.5	23.5
	0.00110	81.9	79.3	24.9
	0.00132	79.3	76.7	14.9

Electrochemical impedance spectroscopy (EIS) measurements

The corrosion of C-steel in 1 NH_2SO_4 in the presence and absence of the investigated cefixime was investigated by EIS method at 25ºC after30 min immersion. Nyquist plots in the absence and presence of investigated cefixime are presented in Figure (7), also Bode plots are presented in Figure (8).It is apparent that Nyquist plots show a single capacitive loop, both in uninhibited and inhibited solutions. The impedance data of C- steel in 1 N H_2SO_4 are analyzed in terms of an equivalent circuit model (Fig. 9) 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}[42] due to the charge transfer reaction. For the Nyquist plots it is obvious that low frequency data are on the right side of the plot and higher frequency data are on the left. This is true for EIS data where impedance usually falls as frequency rises (this is not true for all circuits). The capacity of double layer (C_{dl}) can be calculated from the following equation:

$$C_{dl} = 1/2\pi f_{max} R_{ct} \qquad (11)$$

Where, f_{max} is the maximum frequency. The parameters obtained from impedance measurements are given in Table (7). It can see from Table (7) that the values of charge transfer resistance R_{ct} increase with cefixime concentration [43]. In the case of impedance studies, % IE increases with cefixime concentration. It is also noted that the C_{dl} values tend to decrease when the concentration of cefixime increases. This decrease in C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that this cefixime molecules function by adsorption at the metal/solution interface [44]

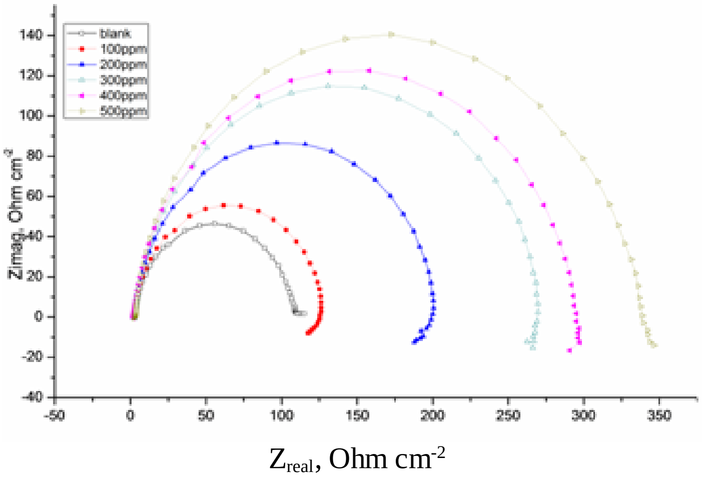


Figure 9 Nyquist plots for carbon steel in 1 N H_2SO_4 solutions in the absence and presence of different concentrations of cefixime at 25ºC

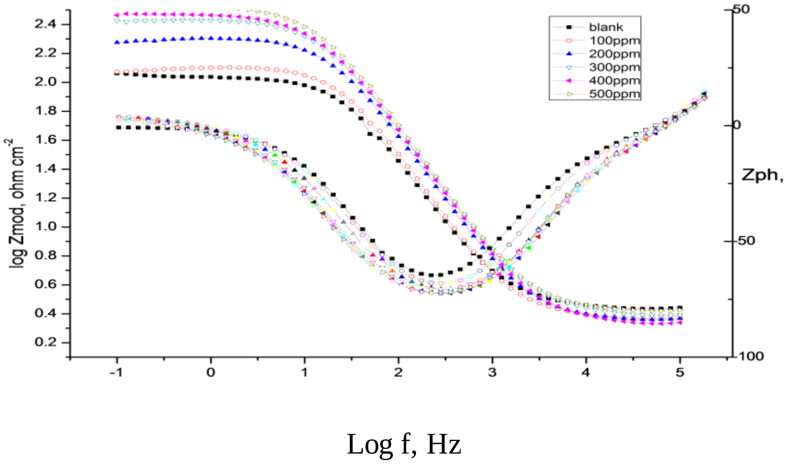


Figure 10 The Bode plot for carbon steel in 1 N H_2SO_4 solution in the absence and presence of different concentrations of cefixime at 25ºC

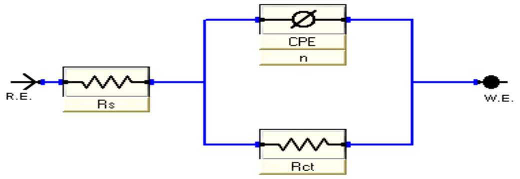


Figure 11 Equivalent circuit model used to fit the impedance spectra

Table 7 Electrochemical kinetic parameters obtained by EIS technique for the corrosion of carbon steel in 1 N H_2SO_4at different concentrations of cefixime at 25º C

Comp.	Conc., ppm	C_{dl}, μFcm^{-2}	R_{ct}, Ω cm^2	θ	% IE
blank	0.00	62.57	107.4	0.0	0.0
Cefixime	100	53.7	122.5	0.123	12.3
	200	41.7	196	0.452	45.2
	300	39.42	267.4	0.598	59.8
	400	39.75	290.7	0.631	63.1
	500	37.24	332.9	0.677	67.7

Electrochemical frequency modulation (EFM) measurements

In corrosion research, it is known that the corrosion process is non-linear in nature, a potential distortion by one or more sine waves will generate responses at more frequencies than the frequencies of applied signal. Virtually no attention has been given to the intermodulation or electrochemical frequency modulation. However, EFM showed that this non-linear response contains enough information about the corroding system so that the corrosion current can be calculated directly. Electrochemical frequency modulation (EFM) is non-destructive corrosion measurement technique that can directly give values of corrosion current without prior knowledge of Tafel constants. In this technique current responses due to a potential perturbation by one or more sine waves are measured at more frequencies than the frequency of the applied signal, for example at zero harmonic and intermodulation frequencies [45].The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement [181]. The results of EFM experiments are a spectrum of current response as a function of frequency. The spectra contain current responses assigned for harmonical and intermodulation current peaks. The results of EFM experiments are a spectrum of current response as a function of frequency. The spectrum is called the intermodulation spectrum and examples for the absence and presence of 500 ppm cefixime to 1 N H_2SO_4 acid solution for C-steel are shown in Figs. (12 and 13) respectively. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors (CF-2 and CF-3). These electrochemical parameters were simultaneously determined and are listed in Table (8). As can be seen from this Table, the corrosion current density decreases in the presence of cefixime than in its absence. The causality factors also indicate that the measured data are of good quality.

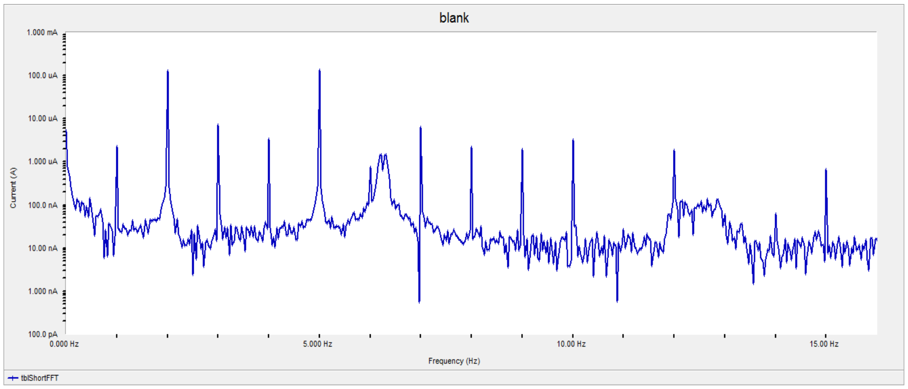


Figure 12 Intermodulation spectrum for carbon steel in 1 N H_2SO_4 solutions without inhibitor at 25ºC

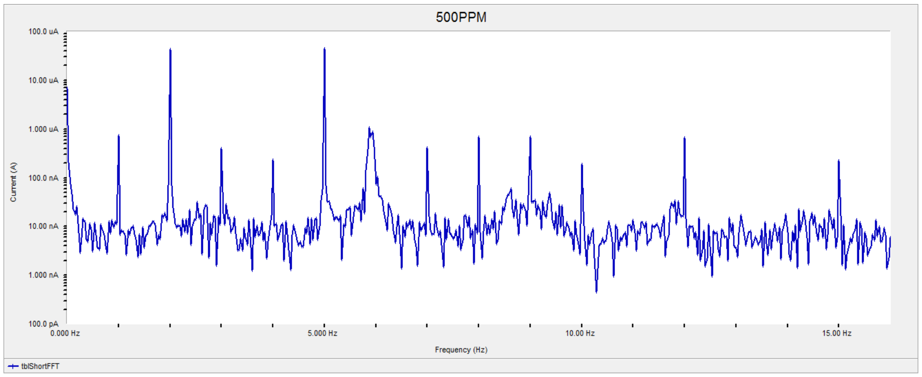


Figure 13 Intermodulation spectrum for carbon steel in 1 N H_2SO_4 solutions with500ppm inhibitor at 25ºC

Table 8 Electrochemical kinetic parameters obtained by EFM technique for carbon steel in 1 N H_2SO_4 solutions with different concentrations of cefixime

Comp.	[Inh] ppm	i_{corr}, μA cm^{-2}	β_a, mV dec^{-1}	β_c, mV dec^{-1}	CF-2	CF-3	CR, mpy	θ	% IE
blank	0.0	190.8	83	112	2.030	2.919	85.08	-	-
Cefixime	100	169.8	85	102	2.035	2.956	75.74	0.110	11.0
	200	106.8	86	97	2.050	3.001	47.61	0.440	44.0
	300	77.64	89	95	2.185	2.899	34.62	0.593	59.3
	400	70.95	90	95	2.253	2.927	31.64	0.628	62.8
	500	61.55	90	95	1.941	4.681	27.45	0.677	67.7

Mechanism of corrosion inhibition

An elucidation of inhibition mechanism requires elaborated knowledge of the fundamental interaction amongst the protective compound and the metal surface. Many of the organic corrosion inhibitors have at least one polar unit with atoms of nitrogen, sulphur, oxygen and in some cases phosphorous. It has been reported that the inhibition efficiency decreases in the order to $O < N < S < P$. The polar unit is considered as the reaction center for the chemisorption process. Moreover; the size, orientation, shape and electric charge on the molecule determine the degree of adsorption and therefore; the effectiveness of inhibitor. Increase in inhibition efficiencies with the increase of concentration of cefixime shows that the inhibition action is due to adsorption on the carbon steel surface. Following are the types of adsorption that may take place at metal/solution interface:(a) Electrostatic attraction between the charged molecules and charged metal(b) Interaction of unshared electron pairs in the molecule with the metal(c) Interaction of p-electrons with the metal(d) Combination of (a) and (c) [54].

In acidic solution, cefixime can be protonated easily. Physical adsorption may take place due to electrostatic interaction between protonated molecule and the metal. Co-ordinate covalent bond formation between electron pairs of unprotonated atoms and metal surface can take place [55]. In addition, cefixime molecule is chemically adsorbed due to interaction of π-orbitals with metal surface. In the present study, the value of ΔG°_{ads} is -30 kJ mol $^{-1}$, hence, showing that adsorption of cefixime molecules on the surface of carbon steel take place through both physical as well as chemical process. Nevertheless, it is clear from the results of effect of temperature that the IE values decreased at higher temperatures, thus, suggested that adsorption of cefixime does not favor at higher temperatures. It indicates that cefixime adsorbed predominantly by physical adsorption on carbon steel surface.

Conclusions

Cefixime acts as a good save inhibitor for the corrosion of carbon steel in 1 NH_2SO_4. The inhibition efficiency of cefixime decreased with temperature, which leads to an increase in activation energy of corrosion process. The adsorption of cefixime follows Langmuir`s adsorption isotherm. The adsorption process is spontaneous and exothermic, accompanied by an increase of entropy. Potentiodynamic polarization curves reveals that cefixime is a mixed-type inhibitor. The results obtained from different experimental studies are in good agreement.

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