

# Ceftriaxone: a novel corrosion inhibitor for mild steel in hydrochloric acid

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**Abstract** Corrosion inhibition of mild steel in 1 N HCl by Ceftriaxone was studied by polarization resistance, Tafel polarization, EIS, and weight loss measurement. The inhibitor showed more than 90% inhibition efficiency at optimum concentration of 400 ppm. Results obtained revealed that inhibition occurs through adsorption of the drug on the metal surface without a modification of the mechanism of the corrosion process. Potentiodynamic polarization suggests that this is a mixed type of inhibitor. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition. Thermodynamic parameters such as  $E_a$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$  and  $Q$  were calculated to investigate the mechanism of inhibition. All the investigations suggested that the compound follows the Langmuir adsorption isotherm.

**Keywords** Mild steel · Corrosion inhibition · Weight loss · EIS · Drug

## 1 Introduction

Corrosion inhibition of mild steel is a matter of theoretical as well as practical importance [1]. Acids are widely used in industries such as pickling, cleaning, descaling, etc., and because of their aggressiveness, inhibitors are used to reduce the rate of dissolution of metals. Compounds containing nitrogen, sulphur, and oxygen have been reported as inhibitors [2–7]. The efficiency of an organic compound

as an inhibitor is mainly dependent upon its ability to get adsorbed on a metal surface, which consists of the replacement of a water molecule at a corroding interface. The adsorption of these compounds is influenced by the electronic structure of inhibiting molecules, the steric factor, aromaticity, and electron density at the donor site, the presence of functional group such as  $-\text{CHO}$ ,  $-\text{N}=\text{N}$ ,  $\text{R}-\text{OH}$ , etc., molecular area, and molecular weight of the inhibitor molecule [8–11].

A large number of organic compounds are known to be applicable as corrosion inhibitors for mild steel [2–7, 12, 13]. However, only a few non-toxic and eco-friendly compounds have been investigated as corrosion inhibitors. Tryptamine, succinic acid, L-ascorbic acid, sulfamethoxazole, and cefatrexyl, were found to be effective inhibitors for acid environments. Dithiobiurets exhibited the best performance towards the corrosion of mild steel in HCl solutions and showed much less toxicity [14–19]. The inhibitive effect of four antibacterial drugs, namely ampicillin, cloxacillin, flucloxacillin, and amoxicillin towards the corrosion of aluminum was investigated [20]. The inhibition action of these drugs was attributed to blocking the surface via formation of insoluble complexes on the metal surface.

Ceftriaxone is the commercial name of (6*R*,7*R*,*Z*)-7-(2-(2-aminothiazol-4-yl)-2-(methoxyimino)acetamido)-3-((6-hydroxy-2-methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-ylthio)methyl)-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylic acid. Ceftriaxone is a third-generation cephalosporin antibiotic. Like other third-generation cephalosporins, it has broad spectrum activity against Gram-positive and Gram-negative bacteria.

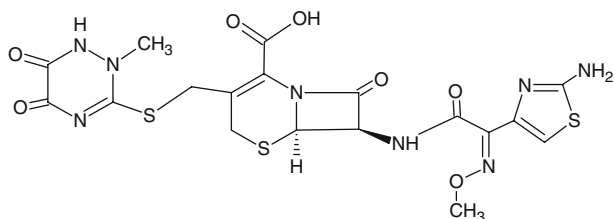
The objective of this study is to investigate the corrosion behavior of mild steel in 1 N HCl solution at 35°C in the presence of Ceftriaxone using weight loss, polarization

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resistance, Tafel polarization, and electrochemical impedance techniques. The effects of temperature, acid concentration, and immersion time were also studied. Several isotherms were tested for their relevance in describing the adsorption behavior of the compounds studied.

## 2 Experimental

The mild steel strips having composition (wt%): C 0.14, Mn 0.035, Si 0.17, S 0.025, P 0.03 and balance Fe were used for weight loss as well as electrochemical studies. The aggressive solution of hydrochloric acid (AR grade) is used for all studies. Ceftriaxone was purchased from a medicine shop and is manufactured by Endeavour, Lupin Ltd. CST road Kalina, Santacruz (East), Mumbai, India. The compound is in its purest state. Its chemical structure is shown as follows:



All the concentrations of the inhibitor taken for weight loss and electrochemical study were taken in ppm by weight. The weight loss study was done on mild-steel strips measuring  $5.0 \times 2.0 \times 0.025$  cm. The weight loss study was carried out at  $35^\circ\text{C}$  for 3 h in 1 N HCl solution. The inhibition efficiency (IE %) was determined by the following equation:

$$\text{IE (\%)} = \frac{W_o - W_i}{W_o} \times 100$$

where  $W_o$  and  $W_i$  is the weight loss value in absence and presence of inhibitor.

The electrochemical studies were made using a three-electrode cell assembly at room temperature [21, 22]. The working electrode was a mild steel of above composition of  $1 \text{ cm}^2$  area and the rest being covered by using commercially available lacquer. A large rectangular platinum foil was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was polished with different grades of emery papers, washed with water, and degreased with acetone. Polarization and impedance studies were carried out using the Gamry Potentiostat/Galvanostat (model 300) with EIS software, Gamry-Instruments Inc., USA. The linear polarization study were carried out from cathodic potential of

$-0.02 \text{ V}$  versus OCP to an anodic potential of  $+0.02 \text{ V}$  versus OCP at a sweep rate  $0.125 \text{ mV s}^{-1}$  to study the polarization resistance ( $R_p$ ). The Tafel polarization was carried out from cathodic potential of  $-0.25 \text{ V}$  versus OCP to an anodic potential of  $+0.25 \text{ V}$  versus OCP at a sweep rate  $0.5 \text{ mV s}^{-1}$  to study the effect of the inhibitor on mild steel corrosion. The linear Tafel segment of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities ( $I_{\text{corr}}$ ). The corrosion IE (%) was evaluated from the measured  $I_{\text{corr}}$  values using the relationship:

$$\text{IE (\%)} = \frac{I_{\text{corr}}^o - I_{\text{corr}}^i}{I_{\text{corr}}^o} \times 100$$

where,  $I_{\text{corr}}^o$  and  $I_{\text{corr}}^i$  are the corrosion current densities in the absence and presence of various concentrations of the inhibitor. The impedance studies were carried out using ac signals of 10 mV amplitude for the frequency spectrum from 100 kHz to 0.01 Hz. The charge transfer resistance values were obtained from the diameter of the semi circles of the Nyquist plots. The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation

$$\text{IE} = \frac{(1/R_t^o) - (1/R_t^i)}{(1/R_t^o)} \times 100$$

where,  $R_{\text{ct}}^o$  and  $R_{\text{ct}}^i$  are the charge transfer resistance in absence and in presence of inhibitor. The interfacial double-layer capacitance ( $C_{\text{dl}}$ ) values have been estimated from the impedance value using bode plot by the formula

$$|Z| = \frac{1}{2\pi f C_{\text{dl}}}$$

## 3 Results and discussion

### 3.1 Weight loss study

The value of percentage inhibition efficiency (% IE) and corrosion rate (CR) obtained from the weight loss method at different concentrations of Ceftriaxone in 1 N HCl at  $35^\circ\text{C}$  are summarized in Table 1. The variation of inhibition efficiency with an increase in inhibitor concentrations is shown in Fig. 1a. It was observed that Ceftriaxone inhibits the corrosion of mild steel in HCl solution, at all concentrations used in study, i.e., 50–500 ppm. Maximum inhibition efficiency has been shown at 400 ppm concentration of the inhibitor in 1 N HCl at  $35^\circ\text{C}$ . It is evident from Table 1 that the corrosion rate decreases from 44.85 to 4.43 mm/year with the addition of 400 ppm of Ceftriaxone.

**Table 1** Corrosion parameters for mild steel in aqueous solution of 1 N HCl in the absence and presence of different concentrations of inhibitors from weight loss measurements at 35°C for 3 h

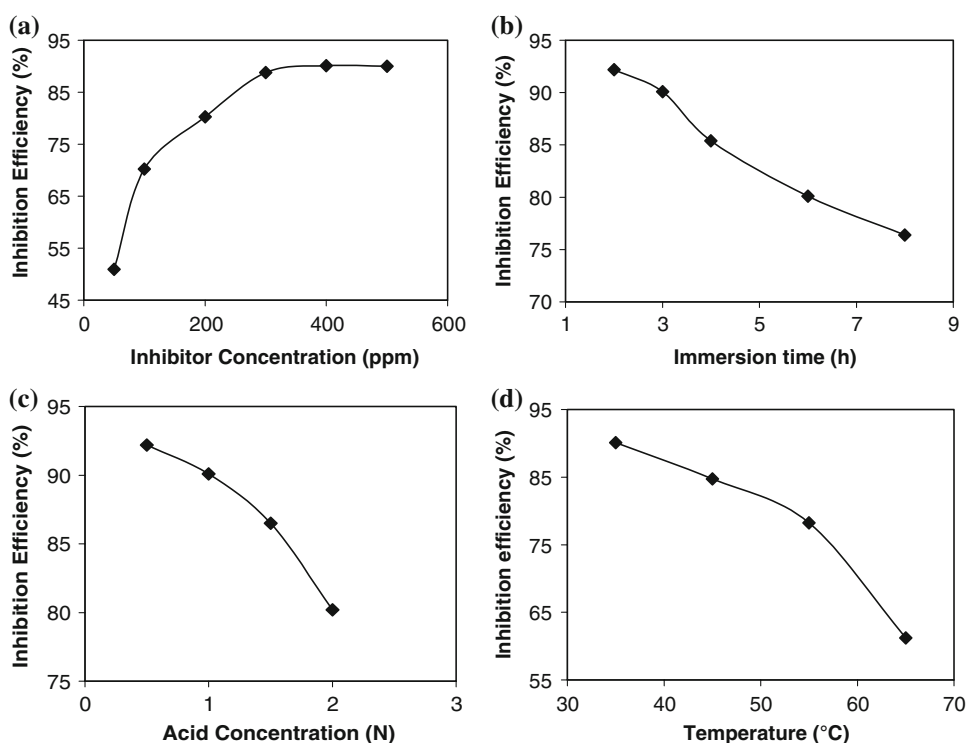
Inhibitor concentration (ppm)	Weight loss (mg)	Inhibition efficiency (%)	Corrosion rate (mmpy)
Blank	241.5	–	44.85
50	118.5	50.93	21.98
100	71.9	70.24	13.34
200	47.6	80.27	8.83
300	27.0	88.81	5.00
400	23.9	90.10	4.43
500	24.2	90.00	4.48

The influence of solution temperature on inhibition efficiency with optimum concentration of ceftriaxone (i.e., 400 ppm) is shown in Fig. 1d. It is observed that inhibition efficiency decreases with an increase in temperature from 35 to 65°C. The decrease in inhibition efficiency with temperature may be attributed to desorption of the inhibitor molecule from metal surface at higher temperature [23].

### 3.2 Polarization resistance

The polarization resistance ( $R_p$ ) values of mild steel in 1 N HCl increases from 13.99  $\Omega$  of the blank to 154.6  $\Omega$  of 400 ppm concentration of Ceftriaxone (Table 2). The

**Fig. 1** Variation of inhibition efficiency in 1 N HCl on mild steel of surface area 20.35 cm<sup>2</sup> with different concentrations of Ceftriaxone inhibitor (a), different immersion time (b), different acid concentration (c), and different temperature range (d)



The effect of immersion time on the inhibition efficiency with optimum concentration of Ceftriaxone (i.e., 400 ppm) is shown in Fig. 1b. It is found that the inhibition efficiency decreases with an increase in immersion time from 2 to 8 h. This suggests that desorption of the inhibitor molecule from metal surface increasing the immersion time.

The variation of inhibition efficiency with increase in acid concentration from 0.5 to 2.0 N with optimum concentration of Ceftriaxone (i.e., 400 ppm) is shown in Fig. 1c. It is clear that a change in acid concentration from 0.5 to 2.0 N inhibition efficiency varies from 92.2 to 80.2%. This change in the inhibition suggests that the compound is not much effective in corrosion inhibition in acid solution at higher concentration of the acid solution.

increase in the  $R_p$  value suggests that the inhibition efficiency increases with the increase in the inhibitor concentration.

**Table 2** Polarization parameters for the corrosion of mild steel in 1 N HCl in absence and presence of different concentrations of inhibitor

Inhibitor concentration (ppm)	$R_p$ ( $\Omega$ )	IE (%)	CR (mmpy)
Blank	13.99	–	14.41
100	45.80	69.45	4.40
200	93.10	84.97	2.17
300	131.10	89.33	1.53
400	154.60	90.95	1.30

### 3.3 Tafel polarization

Figure 2 shows the Tafel polarization curve for mild steel in 1 N HCl with addition of various concentrations of Ceftriaxone. The important corrosion parameters derived from these curves are presented in Table 3. From Table 3, it is evident that it is clear that the corrosion current ( $I_{\text{corr}}$ ) value decreases from 1,540 to 114  $\mu\text{A cm}^{-2}$  with the highest concentration of Ceftriaxone (400 ppm). The addition of Ceftriaxone does not alter the value of  $E_{\text{corr}}$  significantly, indicating the mixed type of inhibiting behavior of the inhibitors.

### 3.4 Electrochemical impedance spectroscopy

Electrochemical impedance measurements were carried out over the frequency range from 10 kHz to 0.01 Hz at open circuit potential. The simple equivalent Randle circuit for studies is shown in Fig. 3, where  $R_{\Omega}$  represents the solution and corrosion product film resistance, the parallel combination of resistor,  $R_t$  and capacitor  $C_{\text{dl}}$  represents the corroding interface. The Nyquist representations of impedance behavior of mild steel in 1 N HCl with and without addition of various concentrations of Ceftriaxone are given in Fig. 4. The existence of a single semi circle showed the single charge transfer process during dissolution, which is unaffected by the presence of inhibitor molecules. It is seen that the addition of the inhibitor increases the values of  $R_{\text{ct}}$  and reduces the  $C_{\text{dl}}$ . The decrease in  $C_{\text{dl}}$  is attributed to an increase in thickness of the electronic double layer [24]. The increase in the  $R_{\text{ct}}$  value is attributed to the formation of protective film on the metal–solution interface [25, 26]. These observations suggest that Ceftriaxone molecules function by adsorption at

the metal surface and thereby causing a decrease in the  $C_{\text{dl}}$  values and an increase in the  $R_{\text{ct}}$  values. The charge transfer resistance ( $R_{\text{ct}}$ ) and the interfacial double-layer capacitance ( $C_{\text{dl}}$ ) derived from these curves are given in Table 4.

### 3.5 Adsorption isotherm and thermodynamic parameter

The degree of surface coverage ( $\theta$ ) for optimum concentration of inhibitor in 1 N HCl at 35–65°C for 3 h of immersion time has been evaluated from weight loss values. The data were tested graphically by fitting to various isotherms. A plot of  $\log(\theta/1-\theta)$  vs.  $1/T$  is given in Fig. 5a. The plot gives the values for calculating heat of adsorption ( $Q$ ) with a slope  $(-Q/2.303R)$ . The values for heat of adsorption are included in Table 5. Since the values of heat of adsorption for the inhibitor is less than  $-40 \text{ KJ mol}^{-1}$ , hence physical adsorption occurs [27].

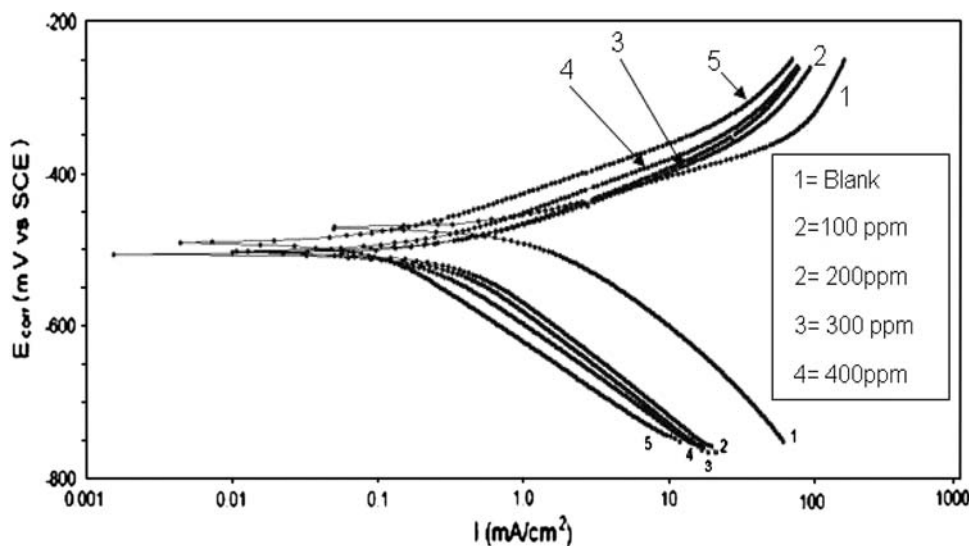
It has been reported by a number of authors [28–30] that in acid solution, the logarithm of the corrosion rate is a linear function with  $1/T$  (Arrhenius equation):

$$\log(\text{rate}) = \frac{-E_a^\circ}{2.303RT} + A$$

where,  $E_a^\circ$  is the apparent effective activation energy,  $R$  is the general gas constant, and  $A$  is the Arrhenius pre-exponential factor. A plot of the log of corrosion rate obtained by weight loss measurement versus  $1/T$  gave a straight line as is shown in Fig. 5b. The values of activation energy ( $E_a^\circ$ ) obtained from the slope of the lines are given in Table 5.

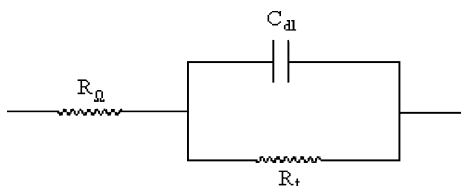
An alternative formula of the Arrhenius equation is the transition state equation [31]:

**Fig. 2** Tafel polarization behavior of mild steel in 1 N hydrochloric acid with different concentration range of Ceftriaxone



**Table 3** Tafel polarization parameters for the corrosion of mild steel in 1 N HCl in the absence and presence of different concentration (0–400 ppm) of inhibitors

Inhibitor concentration (ppm)	$E_{\text{corr}}$ (mV vs. SCE)	ba (mV dec <sup>-1</sup> )	bc (mV dec <sup>-1</sup> )	$I_{\text{corr}}$ (μA cm <sup>-2</sup> )	IE (%)	CR (mmpy)
Blank	-470	65.5	107.1	1,540	–	17.86
100	-503	73.3	152.7	390	74.68	4.53
200	-506	57.3	106.9	166	89.22	1.94
300	-503	64.1	118.9	161	89.54	1.86
400	-491	66.6	140.0	114	92.59	1.32

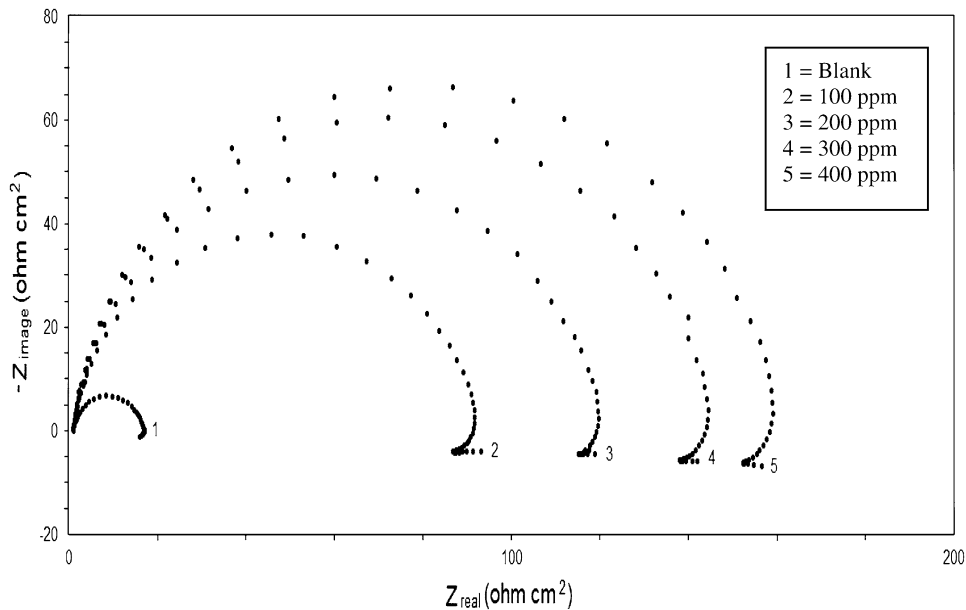


**Fig. 3** Electrical equivalent circuit ( $R_{\Omega}$  = uncompensated solution resistance,  $R_t$  = polarization resistance,  $C_{dl}$  = double-layer capacitance)

$$\text{Rate} = \frac{RT}{Nh} \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(-\frac{\Delta H^\circ}{RT}\right)$$

where  $h$  is Plank’s constant,  $N$  the Avogadro’s number,  $\Delta S^\circ$  the entropy of activation and  $\Delta H^\circ$  the enthalpy of activation. A plot of  $\log(CR/T)$  vs.  $1/T$  gave a straight line (Fig. 5c), with a slope of  $(-\Delta H^\circ/2.303R)$  and an intercept of  $[\log(R/Nh) + (\Delta S^\circ/2.303R)]$ , from which the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  were calculated and listed in

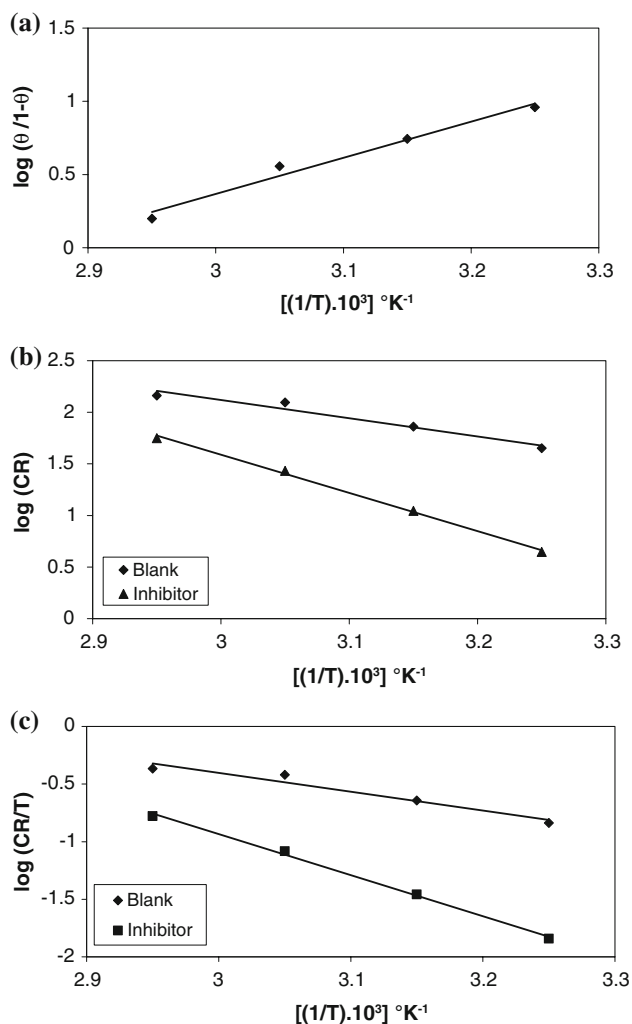
**Fig. 4** Nyquist plot of mild steel in 1 N HCl with different concentration range of Ceftriaxone



**Table 4** Electrochemical impedance parameters for mild steel in 1 N HCl in absence and presence of different concentration of inhibitor

Inhibitor concentration (ppm)	$R_t$ (Ω cm <sup>2</sup> )	$C_{dl}$ (μF cm <sup>-2</sup> )	IE (%)
Blank	19.8	1,555.0	–
100	92.4	311.4	78.57
200	120.2	260.9	83.53
300	144.8	232.5	86.33
400	159.6	207.4	87.59

**Table 5.** The data shows that thermodynamic activation functions ( $E_a^\circ$ ) of the corrosion in mild steel in 1 N HCl solution in the presence of the inhibitor is higher than those in free acid solution, indicating that all the inhibitors lower the inhibition efficiency at higher temperatures [32–34]. The negative values of  $\Delta S^\circ$  and  $\Delta H^\circ$  indicate that the process of adsorption is exothermic, spontaneous, and also increases the system order [35, 36]. The free energy of adsorption ( $\Delta G_{\text{ads}}$ ), calculated using the following equation [23], are given in Table 5.



**Fig. 5** **a** Adsorption isotherm plot for  $\log(\theta/(1-\theta))$  vs.  $1/T$ . **b** Adsorption isotherm plot for  $\log(CR)$  vs.  $1/T$ . **c** Adsorption isotherm plot for  $\log(CR/T)$  vs.  $1/T$

$$\Delta G_{\text{ads}} = -RT \ln(55.5K)$$

$$K = \frac{\theta}{C(1-\theta)}$$

where,  $\theta$  is the degree of coverage on the metal surface,  $C$  is the concentration of inhibitor in mol/L,  $R$  is a constant, and  $T$  is the temperature. The  $\Delta G_{\text{ads}}$  value of the inhibitor is  $16.77 \text{ kJ mol}^{-1}$ . This value is less than  $-40 \text{ kJ mol}^{-1}$ , indicating that all are physically adsorbed on the metal surface [37]. The negative values of  $\Delta G_{\text{ads}}$  indicate the

spontaneous adsorption of the inhibitor on the surface of mild steel [38].

It is well known that organic inhibitors establish inhibition by adsorption onto the metal surface. The adsorption of inhibitors influenced by the chemical structures of organic compounds, nature and surface charge of metal, the distribution of charge in the molecule, and the type of aggressive media [39, 40]. The physical adsorption requires the presence of an electrically charged metal surface and charged species in the bulk of solution. In the case of chemisorption, the process involves charge sharing or charge transfer from the inhibitor molecule to the metal surface. This is possible in both positive and negative charges on this surface. The presence of transition metal having vacant low energy electron orbital and an inhibitor molecule having relatively loosely bound electrons or heteroatoms with lone pair of electrons facilitates this adsorption [41].

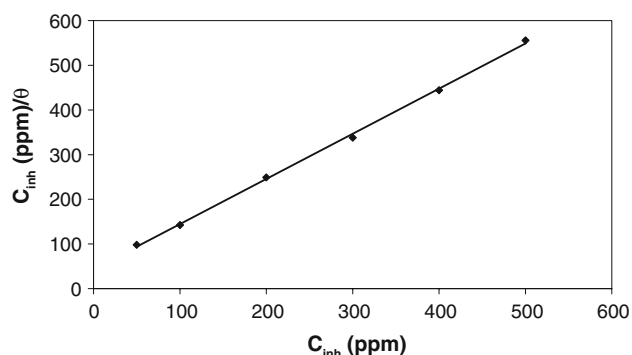
The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior [42]. The most frequently used adsorption isotherms are Langmuir, Temkin, and Frumkin. So several adsorption isotherms were tested to describe the adsorption behavior of Ceftriaxone. A straight line was obtained on plotting  $C_{\text{inh}}$  vs.  $C_{\text{inh}}/\theta$  for the inhibitor used in the study shown in Fig. 6. The degree of surface coverage ( $\theta$ ) for different inhibitor concentrations of Ceftriaxone was evaluated from weight loss data. It was found that Ceftriaxone obeys the Langmuir adsorption isotherm. The plot yields a straight line with slopes of almost equal unity.

### 3.6 Mechanism of inhibition

Corrosion inhibition of mild steel in 1 N HCl by Ceftriaxone can be explained on the basis of molecular adsorption. The compound inhibits corrosion by controlling both the anodic and cathodic reactions. In acidic solutions, the Ceftriaxone exists as a protonated species. These protonated species adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through  $\pi$ -electron of aromatic ring and a lone pair of electrons of nitrogen atom, which decreases anodic dissolution of mild steel [19]. Corrosion inhibition of Ceftriaxone is attributed to the presence of  $\pi$ -electrons, the quaternary nitrogen atom, and the larger molecular size.

**Table 5** Thermodynamic activation parameters for mild steel in 1 N HCl in absence and presence of 400 ppm concentration of Ceftriaxone

Inhibitor concentration (ppm)	$E_a$ (kJ mol $^{-1}$ )	$-\Delta H$ (J mol $^{-1}$ K $^{-1}$ )	$-\Delta S$ (J mol $^{-1}$ K $^{-1}$ )	$-\Delta G$ (kJ mol $^{-1}$ )	$-Q$ (kJ mol $^{-1}$ )
Blank	33.84	31.36	111.41	–	–
400	70.84	68.26	10.59	16.77	47.27



**Fig. 6** Langmuir's adsorption isotherm plots for the adsorption of Ceftriaxone in 1 N HCl on the surface of mild steel

#### 4 Conclusions

- The inhibition efficiency of Ceftriaxone increases with an increase in inhibitor concentration.
- The inhibitor showed maximum inhibition efficiency of 95% at 400 ppm concentration.
- Langmuir adsorption isotherm and impedance studies showed that Ceftriaxone inhibits through its adsorption mechanism.
- Potentiodynamic polarization proved that Ceftriaxone is an efficient commercially available drug having a mixed type of inhibitor property.

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