Int. J. Electrochem. Sci., 6 **(2011)** 146 - 161

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Cefixime: A drug as Efficient Corrosion Inhibitor for Mild Steel in Acidic Media.
Electrochemical and Thermodynamic Studies.

Imran Naqvi[*] *, A. R. Saleemi, S. Naveed*

Department of Chemical Engineering, University of Engg. & Tech., Lahore, Pakistan.
[*]E-mail: aimze74@hotmail.com

Received: 7 August 2010 / *Accepted:* 15 October 2010 / *Published:* 1 January 2011

The corrosion inhibition of mild steel in 1M HCl solution by Cefixime was studied ate temperature range 303–333K by weight loss measurement and electrochemical techniques i.e. Polarization Resistance, Potentiodynamic Polarization and Electrochemical Impedance Spectroscopy (EIS). The results obtained at 30^{o}C divulged that this pharmaceutical compound had established > 90% inhibition efficiency at an optimum concentration of $8.8\times10^{-}$4M. The outcomes show that inhibition takes place by adsorption of the inhibitor on metal surface without altering the mechanism of corrosion process. The adsorption of Cefixime takes place according to Langmuir`s adsorption isotherm. Kinetic parameters (activation energy, $-E_a^o$ and pre-exponential factor, λ) as well as thermodynamic parameters (enthalpy, entropy and free energy of adsorption; S^0_{ads} , ΔH^0_{ads} and ΔG^0_{ads} respectively) were calculated and discoursed. Potentiodynamic polarization studies indicate that Cefixime acts as a mixed type of inhibitor. Data collected from EIS studies has been analyzed to model the appropriate equivalent circuit for better explanation of corrosion inhibition process. The inhibition mechanism of Cefixime has also been discussed.

Keywords: Cefixime, corrosion, mild steel, EIS, Langmuir`s isotherm

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 –CHO, –N=N, R–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.

Cefixime is the commercial name of (6R, 7R) - 7 - [[2 - (2 - amino-1, 3 - thiazol - 4-yl) - 2 - carboxymethyloxyimino)acetyl]amino] - 3 - ethenyl - 8 - oxo - 5 - thia - 1 - azabicyclo [4.2.0]oct-2-ene - 2 carboxylic acid. It is a third generation semi synthetic cephalosporin antibiotic. Cephalosporins are derivatives of 7-aminocephalosporic acid and are closely related to penicillins in structure. Cephalosporins have a six membered sulfur containing ring adjoining a ß lactam ring. Cefixime is effective in a large variety of bacterial infections, such as respiratory tract, ear, skin, gonorrhea, otitis media, and urinary tract infections. The molecular formula of Cefixime is $C_{16}H_{15}N_5O_7S_2$ and molecular weight is 453.4.

A detailed literature review shows no data are available regarding the behavior of Cefixime as inhibitor for protection of mild steel against corrosion. In the present study, the inhibitive properties of this compound are reported for the first time, using weight loss measurement and electrochemical techniques. The inhibition mechanism has been discussed on the basis of these studies.

2. EXPERIMENTAL

The mild steel coupons with dimensions 5cm × 2cm × 0.1cm were cut from a sheet. The chemical composition (wt. %) of these metallic coupons is (C: 0.17, Mn: 0.03, Si: 0.14, S: 0.028, P: 0.033 and Fe: balance).The corrosive solution of hydrochloric acid (AR grade) was used for all studies. Double distilled water was used to prepare the acid solutions. Cefixime, in pure form, was procured from Macter Pharma (Pvt.) Ltd, Karachi, Pakistan. Its chemical structure is shown in Fig. 1.

These coupons had been used for weight loss experiments. Prior to their use, the samples were polished successively by use of SiC papers of 100, 200, 400, 600 and 800 grade; and then thoroughly cleansed with distilled water and then with ethanol. The specimens were dried and kept in a desiccator till their use. All the experiments were performed at room temperature *i.e.* 30 ^{o}C for an immersion time of 3 hrs. The inhibition efficiency (%) and degree of surface coverage (θ) were calculated from the equation (1), (2); where, W_0 and W_i are the values of weight loss without and with addition of inhibitor.

$$I.E\ (\%) = \frac{W_0 - W_i}{W_0} \times 100 \qquad (1)$$

$$\theta = \frac{W_0 - W_i}{W_0} \qquad (2)$$

The electrochemical experiments were performed using a typical three electrode cell at room temperature and naturally aerated conditions.

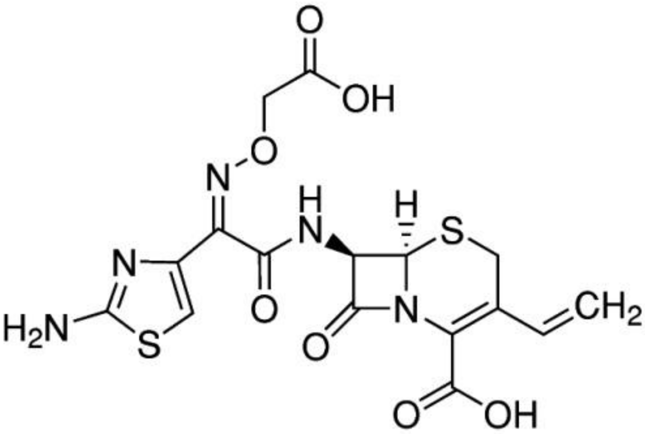

Figure 1. Molecular structure of Cefixime.

The working electrode was mild steel of composition, stated above. The exposed area of each sample was 1 cm^2 and the rest being covered by using commercially available polymeric resin. A glassy carbon rod was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The working electrodes were polished following the procedure, described above. The polarization and impedance studies were conducted in 200 ml 1N HCl solutions using Gamry Potentiostat/Galvanostat (model Reference-600) with DC-105 and EIS-300 software, Gamry-Instruments Inc., USA. Data was analyzed by Echem Analyst 5.58. All the experiments were carried out after the stabilization of the system *i.e.* open circuit potential (OCP) after half an hour of electrode immersion.

The linear polarization experiments were carried out from cathodic potential of −0.02V versus OCP to an anodic potential of +0.02V versus OCP at a sweep rate $0.125 mVs^{-1}$ to study the polarization resistance (R_p). The values of inhibition efficiency (%) were determined from equation (3), where, R_p^i and R_p^0 are polarization resistances with and without addition of inhibitor.

$$I.E\ (\%) = \frac{R_p^i - R_p^0}{R_p^i} \times 100 \qquad (3)$$

The potentiodynamic polarization was carried out from cathodic potential of −0.25V versus OCP to an anodic potential of +0.25V versus OCP at a sweep rate $0.5 mVs^{-1}$ to study the results of inhibitor on mild steel corrosion. The linear sections of anodic and cathodic curves were extrapolated using Tafel technique to obtain the corrosion current densities (I_{corr}). The corrosion inhibition efficiency (%) was evaluated by equation (4), while, I^{0}_{corr} and I^{i}_{corr} are corrosion current densities without and with addition of inhibitor.

$$I.E\ (\%) = \frac{i^{0}_{corr} - i^{i}_{corr}}{i^{0}_{corr}} \times 100 \qquad (4)$$

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 calculated from the diameter of the semi-circles of the Nyquist plots.

The corrosion inhibition efficiency (%) was determined by equation (5), where $R^{'}_{ct}$ and R^{o}_{ct} are the charge transfer resistances in presence and absence of inhibitor. The values of double layer capacitance (C_{dl}) have been calculated by using equation (6), where f_{max} is the frequency at which the imaginary component of the impedance is maximum and R_{ct} is the corresponding value of charge transfer resistance.

$$I.E\ (\%) = \frac{R^{i}_{ct} - R^{0}_{ct}}{R^{i}_{ct}} \times 100 \qquad (5)$$

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \qquad (6)$$

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

The corrosion rates of mild steel in the presence of Cefixime in 1.0 M HCl at different temperatures under study are summarized in Table 1.

From Table 1, it clear that corrosion rates in 1.0 M HCl solution with the addition of Cefixime, decreased as the concentration of inhibitor was changed towards higher side. These results reveal the fact that the adsorption of inhibitor as well as and surface coverage on mild steel increases with increase in inhibitor concentration.

3.1.2. Effect of temperature

The values of inhibition efficiencies at different temperatures obtained from weight loss data for the various inhibitor concentrations in 1.0 M HCl are shown in Fig. 2. It shows that inhibition efficiency decreased at higher temperatures. This behavior indicates desorption of inhibitor molecule [21]. However, at higher inhibitor concentration, the decrease in *I.E* is small.

Table 1. Corrosion rates and values of Inhibition efficiency (%IE) from weight loss measurement for mild steel corrosion in1 M HCl without and with addition of different concentrations of Cefixime at different temperatures.

Inhibitor Conc./ M × 10^{-4}	Temperature/ K	Corrosion Rate / mm $year^{-1}$	I.E / %
Blank	303	43	
	313	62	
	323	108	
	333	156	
1.1	303	15.25	64.4
	313	28.52	54
	323	57.24	47
	333	104.52	33
2.2	303	12.07	72
	313	23.18	62.6
	323	48.60	55
	333	90.50	42
4.4	303	7.76	82
	313	16.74	73
	323	38.90	64
	333	73.30	53
6.6	303	5.61	88
	313	11.80	81
	323	31.32	71
	333	62.40	60
8.8	303	4.31	90
	313	10.54	83
	323	30.24	72
	333	59.30	62

3.1.3. Adsorption isotherm

The mechanism of corrosion inhibition can be explicated on the basis of adsorption behavior. The degrees of surface coverage (θ) for different inhibitor concentrations in 1 M HCl acid in the temperature range (303–333 °K) were assessed by weight loss data. Data were tested graphically by fitting to various isotherms. By far, the experimental data were best fitted by Langmuir`s adsorption isotherm equation [22]:

$$\frac{C_{\mathrm{inh}}}{\theta} = \frac{1}{K} + C_{\mathrm{inh}} \qquad (7)$$

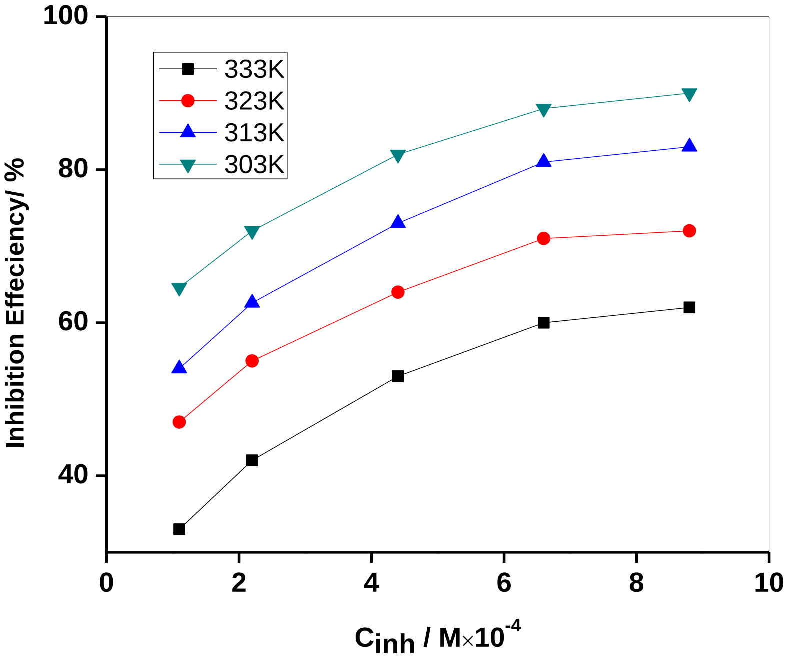

Figure 2. Variation of inhibition efficiency in 1 M HCl on mild steel with different conc. of Cefixime at different temperatures

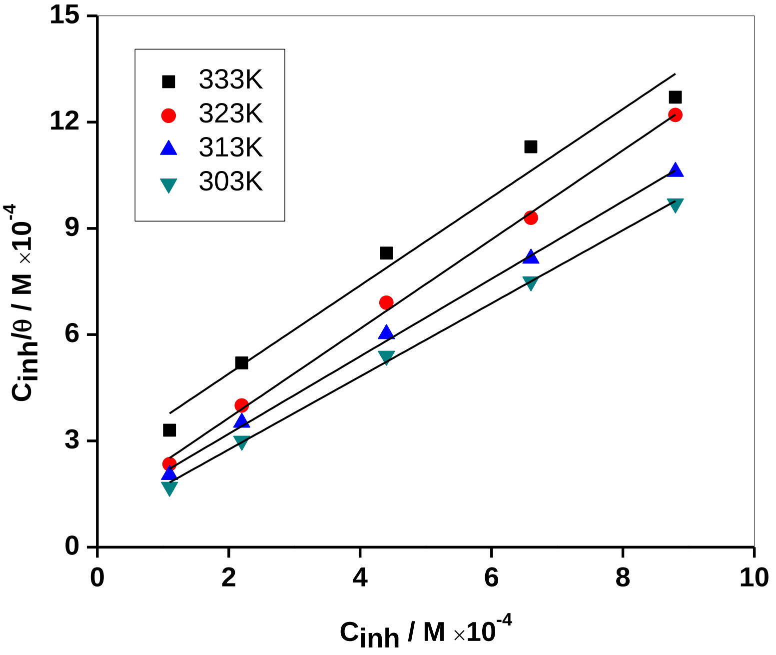

Figure 3. Langmuir's adsorption isotherm plots for the adsorption of Cefixime at different conc. in 1 M HCl on mild steel surface.

Fig. 3 explains the relationship between C_{inh}/θ and C_{inh} at various temperatures. These results depict that all the slopes are close to unity, which indicates that the adsorption of Cefixime follows Langmuir`s adsorption isotherm.

3.1.4. Thermodynamic parameters

Thermodynamic parameters are of great importance to study the inhibition mechanism. The thermodynamic functions for dissolution of mild steel without and with the addition of various concentrations of Cefixime were obtained by applying the Arrhenius equation and the transition state equation [23–26]:

$$\log(CR) = \frac{-E_a^0}{2.303RT} + \log\lambda \qquad (8)$$

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^0}{R}\right)\exp\left(-\frac{\Delta H_a^0}{RT}\right) \qquad (9)$$

Where E_a^o is apparent activation energy, λ; the pre-exponential factor, ΔH_a^0 is the apparent enthalpy of activation, ΔS_a^0 is the apparent entropy of activation, *h*; the Planck's constant and *N* is the Avogadro`s number, respectively. Arrhenius plots of log (CR) vs. 1/T for the blank solution and with different concentrations of Cefixime are shown in Fig. 4.

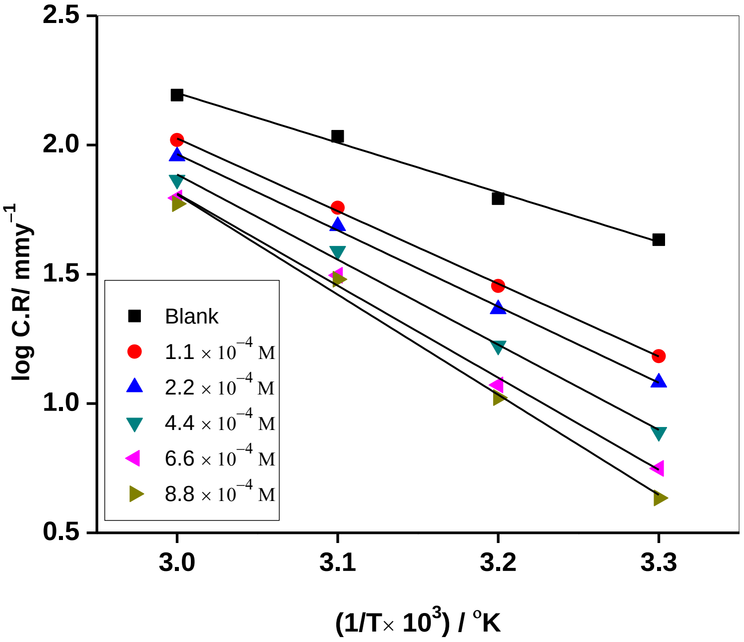

Figure 4. Adsorption isotherm plot for log (CR) vs. 1/T

The parameters were calculated and presented Table 2. The values presented in Table 2 describe that apparent activation energy increased with increasing concentration of Cefixime. This increase in the apparent activation energy may be understood as physical adsorption [17]. Szauer and Brand [27] explained that the increase in activation energy can be ascribed to significant decrease in the adsorption of the inhibitor molecules on the mild 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. According to Eq. (8), corrosion rate (CR) is being effected by both E_a^o and λ. Generally, the influence of E_a^o on the mild steel corrosion was higher than that of λ. However, if the variation in λ was drastically higher than that of E_a^o , the value of λ might be the prevailing and decisive factor for the mild steel corrosion.

Table 2. Kinetic parameters ; E_a^o, ΔH_a^0, ΔS_a^0 for mild steel in 1 M HCl without and with addition of different concentrations of Cefixime.

Inhibitor conc./ $M\times10^{-4}$	E_a^o /KJ mol^{-1}	ΔH_a^0 /KJ mol^{-1}	ΔS_a^0 /J $mol^{-1}K^{-1}$	λ /mg cm^{-2}
0	36.80	36.76	-92.67	9.14×10^{7}
1.1	53.80	51.18	-53.57	2.82×10^{10}
2.2	56.41	53.80	-46.89	6.31×10^{10}
4.4	63.03	60.50	-28.34	5.75×10^{11}
6.6	68.20	65.58	-14.42	3.16×10^{12}
8.8	74.15	71.67	3.64	2.63×10^{13}

In the studied case, E_a^o and λ increased with concentration. As it is apparent from Table 1, the corrosion rate of mild steel decreased while increasing the inhibitor concentration; therefore, it was clear that increment of E_a^o had been the critical factor affecting the corrosion rate of mild steel in 1.0 M HCl. A plot of log (CR/T) vs. 1/T is shown in Fig. Straight lines were obtained with slope equal to $\Delta H_a^0/2.303\ R$ and intercept equal to $(\log R/Nh) + (\Delta S_a^0/2.303R\ )$ from which the values of ΔH_a^0 and ΔS_a^0 were calculated and presented in Table 2. Review of these data divulges that the thermodynamic parameters ΔH_a^0 and ΔS_a^0 of dissolution reaction of mild steel in 1 M HCl in the presence of Cefixime are higher than in the absence of inhibitor. The positive sign of enthalpies ponder the endothermic nature of mild steel dissolution process i.e. dissolution of steel is difficult [28]. Comparing the values of the entropy of activation ΔS_a^0 given in Table 2, it is clear that these values increased positively in the presence of inhibitor than in its absence. The increase of ΔS_a^0 reveals that an increase in disordering takes place from reactant to the activated complex [29]. The relation between constant of adsorption, K_{ads} and standard free energy of adsorption, ΔG_{ads}^0 is as follows:

$$\Delta G_{ads}^0 = -RT\ \ln\ (55.5K_{ads}) \qquad (10)$$

In the above expression, 55.5 is the concentration of water in solution in mol l^{-1}[31]. The values of ΔG_{ads}^0 were calculated from the above equation and summarized in Table 3. Where θ is degree of coverage on the metal surface, C is concentration of inhibitor in mol l^{-1}, R is the molar gas constant and T is temperature. The negative values of ΔG_{ads}^0 indicate that the adsorption process is spontaneous and the adsorbed layer on the mild steel surface is stable. Generally, ΔG_{ads}^0 values of up to −20 kJ mol l^{-1} are consistent with the electrostatic interactions between the charged metal i.e. physiosorption. The values around −40 kJ mol l^{-1} or higher are associated with chemisorption, as a result of sharing or transfer of unshared electron pair or π-electrons of organic molecules to the metal surface to form a coordinate type of bond [30, 31].

Table 3. Thermodynamic parameters for the adsorption of Cefixime in 1 M HCl on mild steel surface at different temperatures.

Temperature/K	ΔG^0_{ads} / KJ mol^{-1}	ΔH^0_{ads} /KJ mol^{-1}	ΔS^0_{ads} /J mol^{-1}K^{-1}
303	−33.52	−49.2	−51.75
313	−32.88	−49.2	−52.14
323	−32.21	−49.2	−52.61
333	−31.95	−49.2	−51.81

The ΔG^0_{ads} value of the inhibitor was found −33.52 kJ mol l^{-1}. This value suggests that Cefixime molecules adsorbed on the metal surface by both physical and chemical process [32–35]. The enthalpy of adsorption was calculated from the following expression:

$$\frac{\Delta G^0_{ads}}{T} = \frac{\Delta H^0_{ads}}{T} + k \qquad (11)$$

The variation of ΔG^0_{ads} /T with 1/T gives a straight line with a slope that equals ΔH^0_{ads} (Fig. 4c). It can be viewed from the figure that ΔG^0_{ads} /T decreases with 1/T in a linear manner. The calculated values are shown in Table 3.

The adsorption heat could be approximately regarded as the standard adsorption heat ΔH^0_{ads} under experimental conditions [24, 36]. The negative sign of ΔH^0_{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 [37]. Typically, the enthalpy of physisorption process is lower than that 41.86 kJ mol l^{-1} while the enthalpy of chemisorption process approaches 100 kJ mol l^{-1} [38]. In this case, the absolute value of enthalpy is −49.2 kJ mol l^{-1}, which is intermediate. Then the standard adsorption entropy ΔS^0_{ads} was obtained using the thermodynamic basic equation:

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads} \qquad (12)$$

The ΔS^0_{ads} values in the presence of inhibitor are large and negative, meaning a decrease in disordering on going from reactants to the metal adsorbed species.

3.2. Linear polarization resistance

Table 3 shows the variation of polarization resistance of mild steel with the addition of Cefixime in the studied media. The polarization resistance (R_p) values of mild steel in 1 M HCl increases from 15.6 Ω cm^2 of inhibitor free solution to 159.2 Ω cm^2 of 8.8×10^{-4} M concentration of inhibitor.

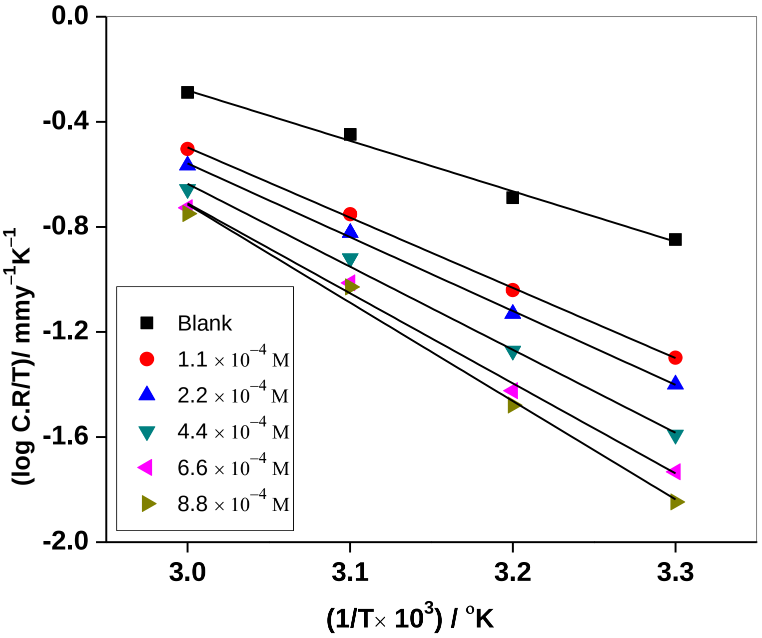

Figure 5. Adsorption isotherm plot for log (CR/T) vs. 1/T

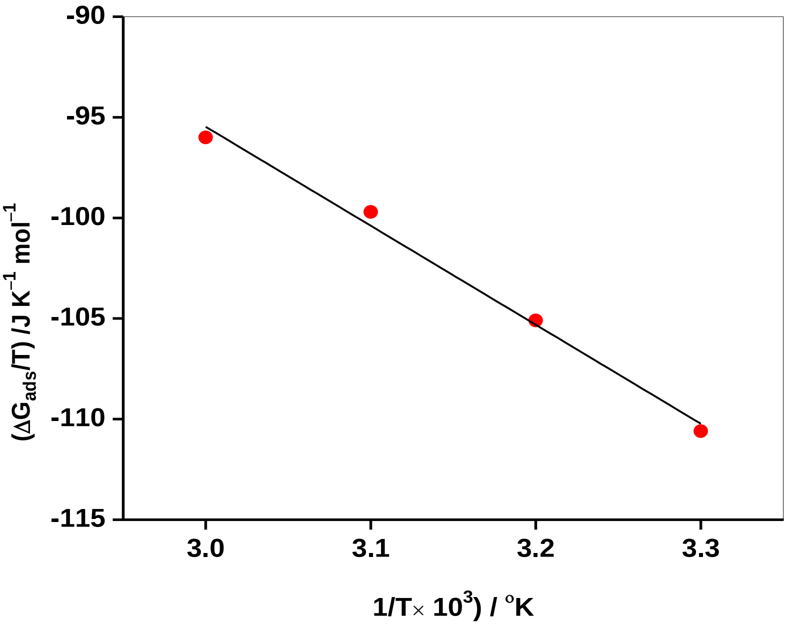

Figure 6. Adsorption isotherm plot for ΔG_{ads}/T vs. 1/T.

3.3. Tafel polarization

Fig. 4 shows the Tafel polarization curves for mild steel in 1 N HCl with the addition of various concentrations of Cefixime. The important corrosion parameters derived from these curves are presented in Table 3. From Table 3 it is clear that the corrosion current density (I_{corr}) value decreases from 1370 to 122 μA cm^2 with the addition of optimum concentration of Cefixime. It is seen from

Table 3 that cathodic and anodic Tafel slope values βa and βc are not very much affected with addition of inhibitor as compared to the blank solution. It indicates that this inhibitor adsorbs on metal surface by simply blocking the active sites and the mechanism of anodic and cathodic reactions is unaffected. However, a shift of corrosion potential (E_{corr}) towards cathodic side *i.e.*−472 to −495 mV was established. The classification of a compound as an anodic or cathodic inhibitor is feasible when the corrosion potential displacement is at least 85mV in relation to that one measured for the blank solution [39]. The addition of Cefixime does not alter the value of E_{corr} significantly indicating the mixed type of inhibiting behavior of the added inhibitor.

Table 4. Electrochemical parameters for corrosion of mild steel in 1 M HCl without and with addition of different concentrations of Cefixime.

Inhibitor conc./	Linear Polarization		Tafel Polarization					EIS			
M×10^{-4}	**R_p/Ω cm^2**	**I.E/ %**	**E_{corr}/mV**	**$β_a$/ mV dec^{-1}**	**$β_c$ /mV dec^{-1}**	**I_{corr}/ μA cm^2**	**I.E/ %**	**Rs/ Ω cm^2**	**R_{ct} /Ω cm^2**	**C_{dl} /μF cm^{-2}**	**I.E/%**
0	15.6		−472	93.5	101.2	1370		**0.28**	16.8	646	
1.1	70.9	77.9	−482	107.4	113.6	250	81.7	**0.52**	78.4	259	61.6
2.2	82.1	81.2	−485	104.1	113.8	221	83.8	**0.74**	116.2	169	85.5
4.4	111.4	85.9	−490	114.2	116.5	198	85.5	**0.84**	138.3	146	87.8
6.6	130.1	88.0	−490	101.3	109.7	172	87.4	**0.81**	173.8	116	90.3
8.8	159.2	90.2	−495	96.3	108.1	114	91.6	**0.80**	208.5	96	91.8

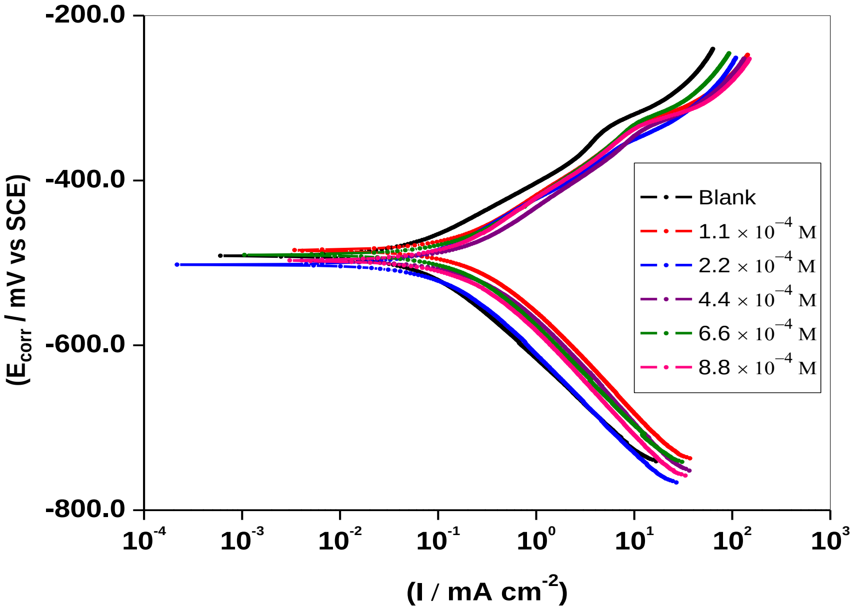

Figure 7. Tafel Polarization behavior of mild steel in 1 M HCl with different concentrations of Cefixime.

3.2. EIS measurements

Electrochemical impedance measurements were carried over the frequency range from 100 kHz to 0.01 Hz at open circuit potential. The simple equivalent Randle circuit for these studies is shown in

Fig. 6, where R_s represents the solution resistance; the parallel combination of resister, R_t and capacitor C_{dl} represents the protective film/ metal interface. The impedance behavior of mild steel in 1 N HCl with and without addition of various concentrations of Cefixime is presented as complex impedance plot (Nyquist plot) in Fig. 7. The existence of single semi circle shows the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. Deviation from perfect circular shape is often referred to the frequency dispersion of interfacial impedance. This anomalous behavior is generally attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena [40–42]. It is seen that addition of inhibitor increases the values of charge transfer resistance (R_{ct}) and reduces the double layer capacitance (C_{dl}).

The decrease in C_{dl} is attributed to increase in thickness of electronic double layer [43]. The increase in R_{ct} value is ascribed to the formation of protective film on the metal/solution interface [44]. These observations suggest that Cefixime molecules function by adsorption at metal surface thereby causing the decrease in C_{dl} values and increase in R_{ct} values. The charge transfer resistance (R_{ct}) and the interfacial double layer capacitance (C_{dl}) derived from these curves are given in Table 3. A small inductive loop can be seen in static conditions for both uninhibited and inhibited solutions. The presence of this low frequency inductive loop may be attributed to the relaxation process obtained by adsorption of species like $(Cl^-)_{ads}$ and $(H^+)_{ads}$ on the electrode surface. It may also be attributed to the re-dissolution of passivated surface [45].

The thickness of the protective layer, d_{org} is related to Cdl by the following equation [46]:

$$C_{dl} = \frac{\varepsilon\varepsilon_0}{d_{org}} \qquad (13)$$

Where, ε_o is the dielectric constant and ε_r is the relative dielectric constant. This decrease in the C_{dl} may result from a reduction in local dielectric constant and/or an increment in the thickness of the electrical double layer. The phenomenon proposed that Cefixime molecules function by adsorption at the metal/solution interface. Thus, the change in C_{dl} values was due to the gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface, decreasing the magnitude of metal dissolution [47].

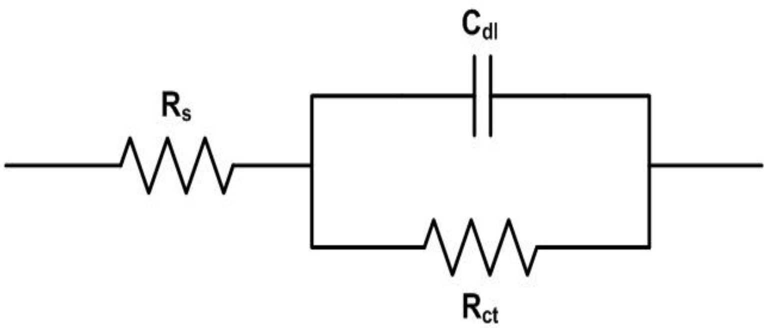

Figure 9. Nyquist plots of mild steel in 1 M HCl with different concentrations of Cefixime.

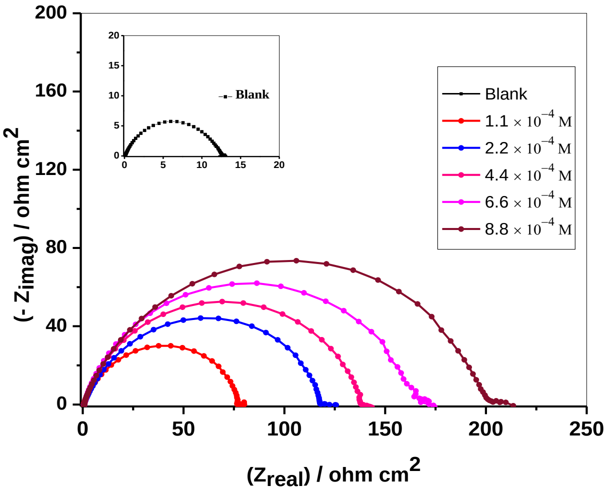

Figure 8. Electrical equivalent circuit (R_s, solution resistance; R_{ct}, charge transfer resistance; C_{dl}, double layer capacitance).

4. MECHANISM OF 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 centre 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 mild 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) [48].

In HCl solution the following mechanism is proposed for the corrosion of iron and steel [49]. According to this mechanism anodic dissolution of iron follows:

$$\mathrm{Fe} + \mathrm{Cl}^- \longleftrightarrow (\mathrm{FeCl}^-)_{\mathrm{ads}}$$

$$(\mathrm{FeCl}^-)_{\mathrm{ads}} \longleftrightarrow (\mathrm{FeCl})_{\mathrm{ads}} + e^-$$

$$(\mathrm{FeCl})_{\mathrm{ads}} \longrightarrow (\mathrm{FeCl}^+) + e^-$$

$$(FeCl^{+}) \longleftrightarrow Fe^{2+} + Cl^{-}$$

The cathodic hydrogen evolution mechanism is:

$$Fe + H^{+} \longleftrightarrow (FeH^{+})_{ads}$$

$$(FeH^{+})_{ads} + e^{-} \longrightarrow (FeH)_{ads}$$

$$(FeH^{+})_{ads} + H^{+} + e^{-} \longrightarrow Fe + H^{2}$$

In acidic solution, carbonyl group, amine group as well as nitrogen atoms in thiazole ring and adjacent carbonyl group can be protonated easily because they all are planar and having greater electron density. Physical adsorption may take place due to electrostatic interaction between protonated molecule and $(FeCl^{-})_{ads}$ species. Co-ordinate covalent bond formation between electron pairs of unprotonated S atom and two N-atoms in thiazole ring and metal surface can take place [50]. In addition, Cefixime molecules are chemically adsorbed due to interaction of π-orbitals with metal surface. This phenomenon is associated with the deprotonation of physically adsorbed protonated molecules. In the present study, the value of ΔG^{0}_{ads} is –35.54 kJ mol $^{-1}$, hence, showing that adsorption of Cefixime molecules on the surface of mild steel take place through both physical as well as chemical process. Nevertheless, it is clear from Table 3 that the values of ΔG^{0}_{ads} 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 mild steel surface.

5. CONCLUSION

Cefixime acts as a good inhibitor for the corrosion of mild steel in 1.0 M HCl. 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 but predominantly cathodic inhibitor. The results obtained from different experimental studies are in good agreement.

References

1. S.A. Ali, M.T. Saeed, S.V. Rahman , *Corros. Sci*. 45 (2003) 253.
2. M. Lagrenee, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, *Corros. Sci*. 44 (2002) 573 .
3. M.A. Quraishi, R. Sardar, *Corrosion* 58 (2002) 748.
4. M.A. Quraishi, M.Athar, H.Ali, *Br Corrosion J* 37 (2002) 155.
5. M.A. Quraishi, , F. A Ansari, *J. Appl. Electrochem*. 33 (2003) 233.
6. M.A. Quraishi., S. Khan, *J. Appl. Electrochem.* 36 (2006) 539.

7. M.A. Quraishi, I.Ahmad, , A. K.Singh, , S. K.Shukla, , B. Lal, , & V.Singh, *Mater. Chem. Phys*. 112 (2008) 1035.
8. F.Bentiss, , M.Lagrenee, , M.Traisnel, , & J. C.Hornez, *Corros. Sci*. 41 (1999) 789.
9. F.B.Growcock, , W.W.Frenier, , & P.A Andreozzi, *Corrosion* 45 (1989) 1007.
10. I.Lukovits, E. Kalman, , G.Palinkas, *Corrosion* 51 (1995) 201.
11. R.C. Ayers, Jr,, N.Hackerman, *J. Electrochem. Soc.* 110 (1963) 507.
12. S. K.Shukla, M. A.Quraishi, , R. Prakash, *Corros. Sci*. 50 (2008) 2867.
13. MA Quraishi, SK Shukla, *Mater. Chem. Phys.* 113 (2008) 685.
14. G.Moretti, F. Guidi, G.Grion, *Corros. Sci*. 46 (2004) 387.
15. F. C.Giacomelli, , C.Giacomelli, M. F Amadori, V.Schmidt, A.Spinelli, *Mater. Chem. Phys*. 83 (2004) 124.
16. E. S.Ferreira, C. Giacomelli, F. C.Giacomelli , A. Spinelli, *Mater. Chem. Phys*. 83 (2004) 129.
17. E. E. F .El Sherbini, *Mater. Chem. Phys*. 60 (1999) 286.
18. M. S.Morad, Corros. Sci. 50 (2008) 436.
19. MA Quraishi, J Rawat, M Ajamal, *J Appl Electrochem* 30 (2000) 745.
20. M.Abdallah, *Corros. Sci.* 46 (2004) 1981.
21. M.Schorr, J.Yahalom, *Corros. Sci.* 12 (1972) 867.
22. X.H. Li, S.D. Deng, G.N. Mu, H. Fu, F.Z. Yang, *Corros. Sci.* 50 (2008) 420.
23. J.O’M. Bockris, A.K.N. Reddy, *Modern Electrochemistry*, vol. 2, Plenum Press, New York, 1977.
24. X.H. Li, S.D. Deng, H. Fu, G.N. Mu, *Corros. Sci*. 50 (2008) 2635.
25. Z. Wei, P. Duby, P. Somasundaran, *J. Colloid Interface Sci*. 259 (2003) 97.
26. A.Ostovari, S.M. Hoseinieh, M. Peikari, S.R. Shadizadeh, S.J. Hashemi, *Corros. Sci*. 51 (2009) 1935.
27. T. Szauer, A. Brand, *Electrochim. Acta* 26 (1981) 1219.
28. N.M. Guan, L. Xueming, L. Fei, *Mater. Chem. Phys*. 86 (2004) 59..
29. E. Khamis, A. Hosney, S. El-Khodary, *Afinidad* 52 (1995) 95.
30. J. Flis, T. Zakroczymski, *J. Electrochem. Soc*. 143 (1996) 2458.
31. E. Khamis, F. Bellucci, R.M. Latanision, E.S.H. El-Ashry, *Corrosion* 47 (1991) 677.
32. F.M. Donahue, K. Nobe, *J. Electrochem. Soc*. 112 (1965) 886.
33. S. Brinic, Z. Grubac, R. Babic, M. Metikos-Hukovic, in*: 8th Eur. Symp. Corros. Inhib.*, vol. 1, Ferrara, Italy, 1995, p. 197.
34. E. Geler, D.S. Azambuja, *Corros. Sci*. 42 (2000) 631.
35. M. Bouklah, N. Benchat, B. Hammouti, A. Aouniti, S. Kertit, *Mater. Lett.* 60 (2006) 1901.
36. T.P. Zhao, G.N. Mu, *Corros. Sci*. 41 (1999) 1937.
37. W. Durnie, R. De Marco, B. Kinsella, A. Jefferson, *J. Electrochem. Soc.* 146 (5) (1999) 1751.
38. S. Martinez, I. Stern, *Appl. Surf. Sci.* 199 (2002) 83.
39. O. L.Riggs, , Jr. (1973). Theoretical aspects of corrosion inhibitors and inhibition. In C. C. Nathan (Ed.), Corrosion inhibitors (pp. 2–27). Houston, TX, USA: The National Association of Corrosion Engineers (NACE).
40. H.Shih, H.Mansfeld, *Corros. Sci.* 29 (1989) 1235.
41. M.Mansfeld, S.Martinez, *J Appl Electrochem* 33 (2003) 1137.
42. M.Elayyachy, A.El Idrissi, B. Hammouti, *Corros. Sci.* 48 (2006) 2470 .
43. M. G.Hosseini, , M.,Ehteshamzadeh, & T. Shahrabi, *Electrochim. Acta*. 52 (2007) 3680.
44. F.Bentiss , M. Traisnel, M. Lagrenee, *Corros. Sci*. 42 (2000) 127.
45. S.Murlidharan, K. L. N Phani, S Pitchumani, S. Ravichandran, *J. Electrocem. Soc.* 142 (1995) 1478.
46. F. Bentiss, B. Mehdi, B. Mernari, M. Traisnel, H. Vezin, *Corrosion* 58 (2002) 399.
47. E. McCafferty, N. Hackerman, *J. Electrochem. Soc*. 119 (1972) 146
48. H. Shorky, M. Yuasa, I. Sekine, R.M. Issa, H.Y. El-Baradie, G.K. Gomma, *Corros. Sci.* 40 (1998) 2173.

49. M. Morad, J. Morvan, J. Pagetti, in: Proceedings of the Eighth European Symposium on Corrosion Inhibitors (8SEIC), Sez V, Suppl. N. 10, Ann. Univ. Ferrara, NS, 1995, p. 159.
50. Ashish Kumar Singh, M.A. Quraishi, *Corros. Sci.* 52 (2010) 152.