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Adsorption Properties and Inhibitive Effect of Antibacterial Drug on Carbon Steel Corrosion in HCl Medium

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The corrosion inhibition of carbon steel in 1.0 M HCl by antibacterial drug named Cephradine (CPD), has been investigated by weight loss and potentiodynamic polarization techniqes. The results showed that CPD is an effective inhibitor for the carbon steel corrosion in acidic solution. The inhibition efficiency increases with increasing inhibitor concentration, while it decreases with the increase in solution temperature. Thermodynamic parameters were calculated and discussed. Adsorption characteristics of the inhibitor has been studied and it is found that cephradine inhibits the corrosion of carbon steel by being adsorbed on the surface of carbon steel by a physical adsorption mechanism. The adsorption of the inhibitor was also found to be spontaneous and consistent with the assumptions of Langmuir adsorption isotherm. Surface analysis using energy dispersive X-ray (EDX) and scanning electron microscope (SEM) was applied to confirm the inhibition efficiency of cephradine.

Key Words: Corrosion inhibition, Cephradine, carbon steel, polarization, adsorption.

The study of carbon steel corrosion phenomena has become an important industrial and academic topic, especially in acid media, this is due to the increased industrial applications of acid solutions. The most important fields of application being acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes[1]. However, the rate of corrosion at which metals are destroyed in acidic media is very high, especially when soluble corrosion products are formed. Therefore, investigating and exploring corrosion inhibitors for steel corrosion in acid solutions is important not only for its academic meaning but also for its practical application[2,3].

Corrosion inhibitors are used to prevent metal dissolution as well as acid consumption[4,5]. Most organic inhibitors are substances with at least one functional group, which considered as the reaction center for the adsorption process. The adsorption of inhibitors is related to the presence of heteroatom as nitrogen[6-9], phosphorus and sulfur[10-12]. Sulphur and nitrogen containing compounds are more effective as corrosion inhibitor in hydrochloric acid[13-15].

Unfortunately most of the organic inhibitors are toxic, very expensive and environmentally unfriendly. Due to increasing environmental awareness and adverse effect of some chemicals, research activities in recent times are geared towards developing cheap, non-toxic and environmentally acceptable corrosion inhibitors[15]. Recently, studies on the use of drug derivatives as corrosion inhibitors have been

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intensified because of their eco-environmental nature[16-18].

The choice of some expired drug derivatives to be 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[19-21].

Cephradine (CPD) is a first generation semi synthetic cephalosporin antibiotic. Cephalosporins are derivatives of 7-aminocephalosporic acid and are closely related to penicillin in structure. Cephalosporins have a six membered sulfur containing ring adjoining a ß-lactam ring.

The objective of this paper is to study the inhibitive action of cephradine on corrosion of carbon steel in hydrochloric acid solution using weight-loss and potentiodynamic polarization techniques. EDX analysis and SEM observations of the electrode surface have been performed in 1.0M HCl solution in the absence and presence of Cephradine to confirm its inhibition efficiency. It was also the purpose of the present work to gain some insight into several adsorption isotherms at different temperatures, in order to determine the thermodynamic functions for the adsorption process and gain more information on the mode of adsorption.

EXPERIMENTAL

Materials and Solutions

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 balance Fe were used for weight loss as well as electrochemical studies. The aggressive solutions, 1.0 M HCl, were prepared by dilution of AR grade 37% HCl in distilled water. The stock solution of Cephradine was diluted to a certain concentration of Cephradine. The inhibitor concentration in the weight loss and electrochemical study was in the range of 3×10^{-4} M to 15×10^{-4} M.

Inhibitor

The studied compound cephradine, is a commercial name of (6*R*, 7R)-7-{[(2*R*)-2-amino-2-(1-cyclohexa-1,4-dienyl) acetyl] amino}-3-methyl-8- oxo-5-thia- 1-azabicyclo [4.2.0] oct-2-ene-2-carboxylic acid , the molecular structure of cephradine is shown in Fig.1. Cephradine is an antibacterial drug, it is an N-S heterocyclic compound containing four oxygen atoms and three nitrogen atoms which could be easily protonated in acid solution, and a great deal of π–electrons exists in this molecule. Stock solution of cephradine was made in the aggressive solution and used for all experimental purposes.

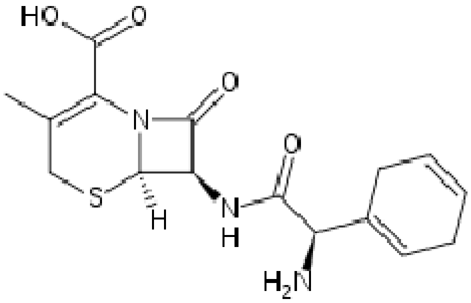

Fig. 1. Molecular structure of Cephradine

Weight loss measurements

Rectangular specimens of carbon steel with dimensions (6cm x 2.5 cm x 0.5 cm) were mechanically polished with 180,400,600 and 1200 grades of emery paper. They were degreased with acetone and rinsed with distilled water two times. Then they were immersed in 0.5 M HCl solution for 10s (chemical method to cleaning rust products), rinsed with distilled water two times and finally dried. The specimens were accurately weighted using an analytical balance accurate to 0.1 mg and then immersed in solution containing 1.0MHCl with and without different concentrations of cephradine and all experiments were carried out in unstirred solutions.. After immersion for 48 hrs, the steel sheets were taken out, rinsed thoroughly with distilled, dried, and weighted, accurately. Duplicate experiments were performed in each and the mean value of the weight loss was reported. The corrosion rate (r) and inhibition efficiency (η %) are calculated as follows[22]:

$$r = (m_1 - m_2)/St \qquad ...(1)$$

$$(\eta\%) = [1 - (r/r^o)] \times 100 \qquad ...(2)$$

where, r and r^o ($gm^{-2}h^{-1}$) are the corrosion rate of steel with and without the addition of cephradine in HCl solution, respectively. The m_1 and m_2 are the weight of steel before and after immersion in solution, respectively, (S) and t (48h) are the surface area of the steel sheet and the corrosion immersion time respectively.

Electrochemical measurements

Electrochemical measurements were investigated in a conventional three electrode cylindrical Pyrex glass cell equipped with thermostat cooling condenser. The working electrode (WE), in the form of a disc cut from carbon steel, had a geometrical area of 1 cm^2 sealed epoxy resin to avoid any infiltration of electrolyte. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrode, respectively. The temperature was thermostatically controlled at room temperature. The working electrode was first immersed in the test solution for establishing a steady state open circuit potential (OCP).

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.

All measurements were made after 30 min. immersion in corrosive media in the absence and presence of inhibitors and the reasonable reproducibility is achieved through repetition.

Surface study

Carbon steel coupons were immersed in 1.0M HCl for 48 hrs in absence and presence of optimum concentration of the studied inhibitor. The surface film formed on the metal specimen was examined by energy dispersive X-ray analysis (EDXA) using X-Max Oxford energy dispersive spectrometer and the SEM examination is carried out using Jeol 5400 scanning electron microscope. The energy of the acceleration beam employed was 30 KV.

RESULTS AND DISCUSSION

Weight loss measurements

Effect of inhibitor concentration

The corrosion rate values of carbon steel in absence and presence of Cephradine in 1.0 M HCl at various temperatures are presented in Table 1. The data reported in Table 1 revealed that, the percent IE of the studied inhibitor increases as the concentration of inhibitor increases and consequently the corrosion rate values in 1.0 M HCl solution containing cephradine, decrease. This result could be attributed to the strong interaction of compound with the metal surface that results in the adsorption of inhibitor molecules .The adsorption amount and the coverage of inhibitor on carbon steel surface increase with increasing the inhibitor concentration[23]. The lone pair of electron on the nitrogen atoms will co-ordinate with the metal atoms of actives sites. The presence of higher electron density in cephradine molecule causes stronger interaction with metal surface. The

Table 1. Corrosion rates and values of inhibition efficiency (η %) from weight loss measurements for carbon steel in 1.0 M HCl without and with addition of different concentrations of cephradine at different temperatures.

Inhibitor Conc.(M$\times 10^{-4}$)	Temp. (K)	Corrosion Rate (mg cm^{-2} h^{-1} $\times 10^{-2}$)	η%
Blank	303	7.84	-
	313	8.60	-
	323	9.60	-
	333	10.0	-
3	303	2.82	64
	313	3.60	58
	323	4.90	49
	333	6.70	37
6	303	2.35	70
	313	3.00	65
	323	4.10	57
	333	5.10	51
9	303	2.00	75
	313	2.60	70
	323	3.60	63
	333	4.40	58
12	303	1.64	79
	313	2.20	75
	323	3.00	69
	333	4.00	62
15	303	1.18	85
	313	1.80	79
	323	2.70	72
	333	3.30	68

nitrogen atoms can donate π–electrons to the metal surface to increase adsorption and hence provide higher inhibition of the corrosion[24].

Effect of temperature

The values of inhibition efficiencies obtained from weight loss measurement for the different inhibitor concentrations in 1.0 M HCl and at different temperatures are shown in Fig. 2. It shows that inhibition efficiency decreased with increasing temperature, which indicates desorption of inhibitor molecule[25].

Adsorption isotherm

Basic information on the interaction between the inhibitor and the carbon steel surface can be provided using the adsorption isotherm. For this purpose, the values of surface coverage (θ) at different concentrations of Cephradine in 1.0 M HCl acid in the temperature range (303–333 K) were calculated to explain the best isotherm to determine the adsorption process from the experimental data obtained. The degree of surface coverage (θ) is calculated from the polarization data using the following equation,

$$\theta = (I^{o}_{corr} - I_{corr})/I^{o}_{corr} \qquad ...(3)$$

where, I^{o}_{corr} and I_{corr} are the corrosion current densities in the absence and in the presence of inhibitor, respectively.

Attempts were made to fit the θ values to various isotherm including Frumkin, Langmuir, Temkin, Freundlich isotherms. By far, the experimental data the results were best fitted by Langmuir adsorption isotherm equation[26]:

$$C_{inh.}/\theta = 1/K_{ads} + C_{inh.} \qquad ...(4)$$

where, K_{ads} is the equilibrium constant of the adsorption process. This isotherm assumes that adsorbed molecules occupy only one site and

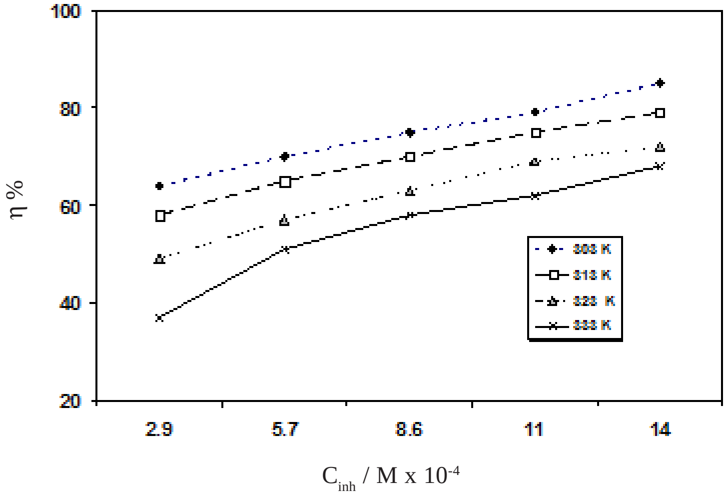

Fig. 2. Variations of inhibition efficiency in 1.0 M HCl on carbon steel with different concentrations of Cephradine at different temperatures.

Table 2. Values of thermodynamic parameters for the adsorption of Cephradine in 1.0 M HCl on carbon steel at different temperatures

Temp (K)	$K_{ads.}$, (mol^{-1})	Slope	R^2	ΔG^{o}_{ads}, ($kJmol^{-1}$)	ΔH^{o}_{ads}, ($kJmol^{-1}$)	ΔS^{o}_{ads}, ($Jmol^{-1}$)
303	5707	1.0839	0.9933	-31.9	-26.2	19.5
313	4789	1.1388	0.9950	-32.5		
323	3485	1.1979	0.9941	-32.7		
333	2179	1.1600	0.9985	-32.4		

Table 3. Values of activation parameters for carbon steel in 1.0 M HCl in the absence and presence of different concentrations of the inhibitor.

Inhibitor Conc. (Mx 10^{-4})	E^o_a (kJ mol^{-1})	ΔH^o_a (kJ mol^{-1})	ΔS^o_a (J mol^{-1})
0	19.9	16.63	-271.0
3	24.9	22.45	-258.7
6	21.4	19.95	-268.5
9	24.3	19.95	-269.3
12	25.4	22.45	-262.9
15	29.5	28.57	-246.4

Table 4. Potentiodynamic polarization parameters for carbon steel in absence and presence of different concentrations of Cephradine

Conc. ($Mx10^{-4}$)	R, (Mmpy)	$E_{corr.}$ (mV)	$I_{corr,}$ (m A cm^{-2})	$B_{a,}$ (mV)	B_c, (mV)	Rp, (Ω cm)	η (%)
0	42.0	-544	3.59	316	-351	15.5	-
3	1.55	-523	0.13	91.1	-137	210	96.3
6	1.45	-519	0.12	89.1	-139	247	96.6
9	1.25	-523	0.11	97.4	-141	282	97.0
12	0.94	-518	0.08	91.9	-137	319	97.8
15	0.76	-516	0.07	86.5	-120	342	98.2

it does not interact with other adsorbed species. Fig. 3a shows the relationship between $C_{inh.}$ /θ and $C_{inh.}$ at temperature ranges studied. These results show that all the linear correlation coefficients (R^2) are almost equal to unity and all the slopes are very close to unity, which indicates that the adsorption of cephradine follows Langmuir adsorption isotherm.

The K_{ads} values can be calculated from the intercept lines on the $C_{inh.}$ /θ axis. This is related to the standard free energy of adsorption (ΔG^o_{ads}) by the following equitation:

$$\Delta G^o_{ads} = -RT \ln (55.5\, K_{ads}) \qquad ...(5)$$

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.

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), while, 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 30°C for carbon steel lies between -31.9 kJ/mol^{-1} and -32.4 kJ/mol^{-1}, which indicate that adsorption of Cephradine molecules on the metal surface involves complex interactions: both physical and chemical process[27,28]. The negative value of ΔG^o_{ads} indicates spontaneous adsorption of the inhibitor on the metal surface. The heat of adsorption (ΔH^o_{ads}) is calculated using the Vant"Hoff equation[29]:

$$\text{Ln } K_{ads} = (-\Delta H^o_{ads} /RT) + \text{constant} \qquad ...(6)$$

To calculate the heat of adsorption, $\ln K_{ads}$ and 1/T were plotted and the plots are given in Fig.3b. From the straight line graph the slope ($-\Delta H^o_{ads}$ /R) and intercept [($-\Delta S^o_{ads}$ /R + ln (1/55.5)] values are calculated. The calculated values of heat of adsorption and entropy are given in Table 2. The adsorption heat could be approximately

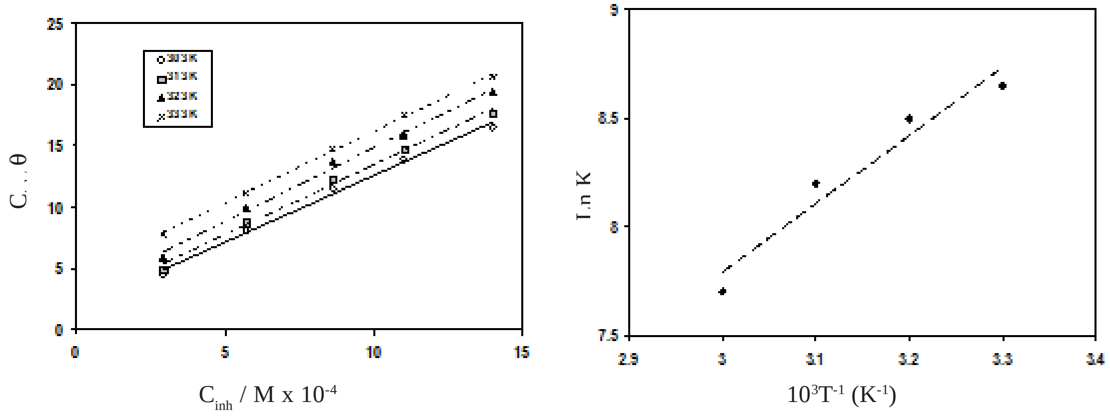

Fig.3. Adsorption isotherm for carbon steel in 1.0 M HCl solution at different temperatures ; (a) Langmuir adsorption isotherm;(b) Vant'Hoff plot for the carbon steel/cephradine/HCl solution.

regarded as the standard adsorption heat under experimental conditions[30,31].The negative sign of ΔH^o_{ads} in HCl solution indicates that the adsorption of the inhibitor molecule is an exothermic process.

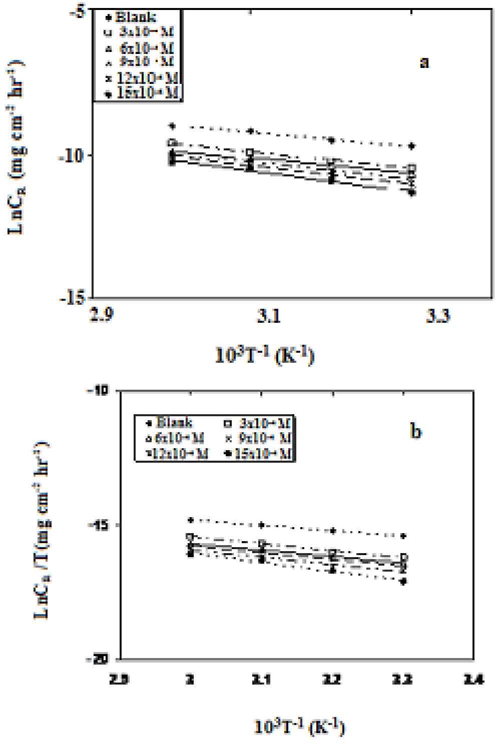

Fig. 4. (a) Adsorption isotherm plot for ln (C_R) vs. 1/T; (b) Adsorption isotherm plot for (lnC_R/T) vs. 1/T at different concentrations of Cephradine in 1.0 M HCl solution.

Generally, an exothermic adsorption process signifies either physisorption or chemisorption while endothermic process is recognized to chemisorption[32]. 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^{-1} [33]. In this case, the absolute value of enthalpy is -26.6 kJ mol^{-1}, which is an intermediate value.

The positive value of ΔS^o_{ads} in the presence of inhibitor is an indication of the increase in solvent entropy. It can be also interpreted with the increase of disorders due to more water molecules which can be desorbed from the metal surface by one inhibitor molecule[34].

Thermodynamic parameters

Thermodynamic parameters have important role in studying the inhibitive mechanism. The thermodynamic functions for dissolution of carbon steel in the absence and in the presence of various concentrations of cephradine were obtained by applying the Arrhenius equation and the transition state equation[35].

The apparent activation energy (E^o_a) of metal dissolution in acid media can be calculated from the Arrhenius equation[36]:

$$\text{Ln } C_R = - E^o_a / RT + A \qquad ...(7)$$

where, E^o_a is the apparent activation energy for the corrosion of carbon steel, R is the universal gas constant; A is the Arrhenius preexponential 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.4a) are given in Table 3.

As a general rule, the higher value 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[37].

In the present study the apparent activation energy increased with increasing concentrations of cephradine. This increase in the apparent activation energy may be understood as physical adsorption[38]. Szauer and Brand[37] 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[36]:

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

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 gave a straight line (Figure 4b) with a slope of ($-\Delta H^{o}_{a}$/2.303R) and an intercept of [log(R/Nh) + (Δ^{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 M HCl in the presence of Cephradine are higher than those in the absence of inhibitor. The trend of the enthalpy values towards positive direction reflects the endothermic nature of steel dissolution process meaning that the dissolution of steel is getting more difficult on addition of the inhibitor[39].

Potentiodynamic polarization measurements

Polarization curves for carbon steel in 1.0M hydrochloric acid without and with addition of different concentrations of the inhibitor are shown in Fig.5. The values of electrochemical parameters associated with polarization measurements, such as corrosion potential (E_{corr}), corrosion current densities (I_{corr}), Tafel slopes (β_a, β_c) and calculated inhibition efficiency (η %) are listed in Table 4. The inhibition efficiency is given by equation following equation[40]:

$$\eta\,\% = (I_o - I_{inh.} / I_o) \times 100 \qquad \ldots(9)$$

where, I_o = corrosion current in absence of the inhibitor; $I_{inh.}$ =corrosion current in presence of inhibitor.

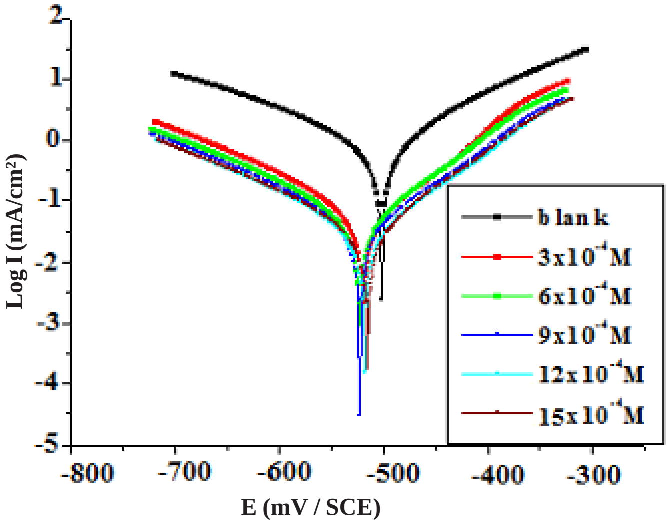

Fig. 5. Anodic and cathodic polarization curves for carbon steel in 1.0 M HCl without and with various concentrations of Cephradine at room temperature.

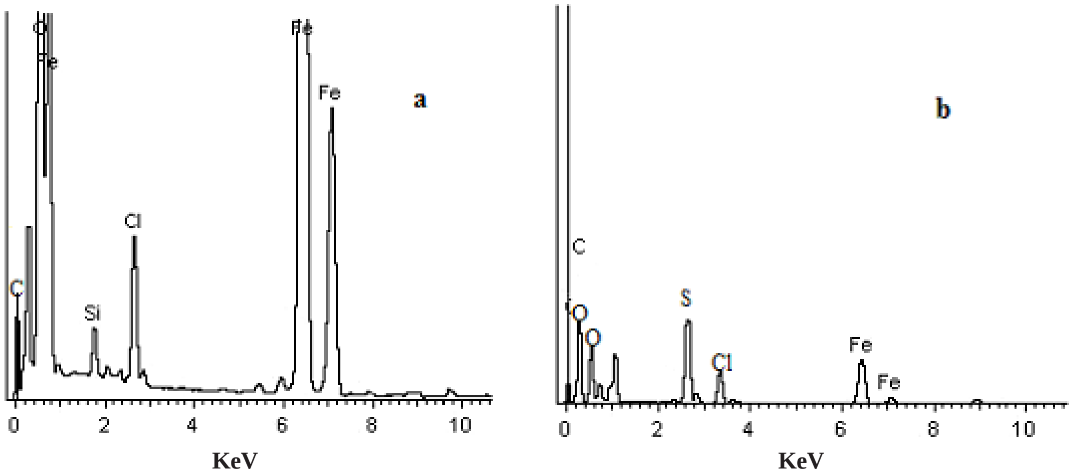

Fig. 6. EDX spectra of carbon steel specimens, (a) After 48 h of immersion in 1.0 M HCl and (b) After 48 h of immersion in 1.0 M HCl containing 15 x 10^{-4} M Cephradine.

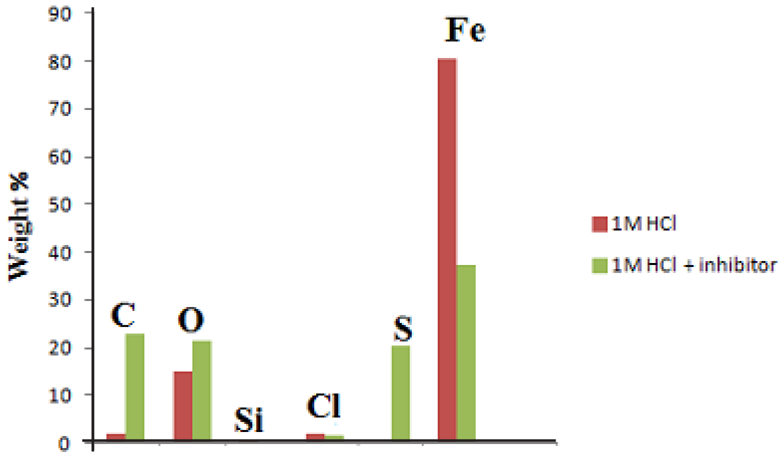

Fig. 7. Concentration of the components of the surface film formed on carbon steel surface in absence and presence of inhibitor.

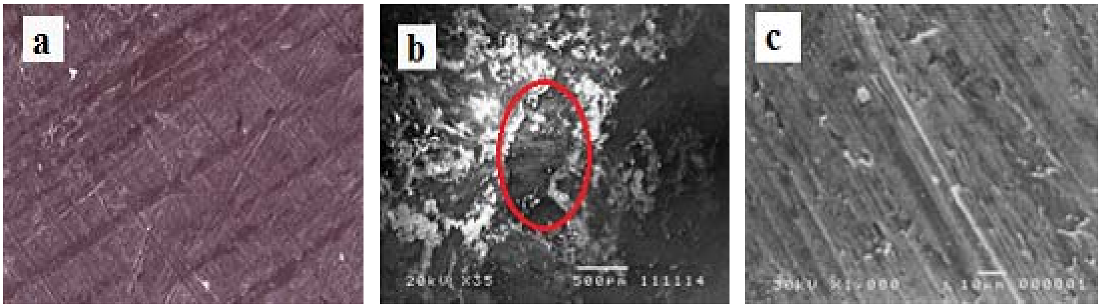

Fig.8. SEM micrographs of carbon steel surface (a) polished surface (b) after immersion in 1.0 M HCl (c) after immersion in 1.0 M HCl+ 15x10^{-4} M cephradine.

Corrosion current density decreases noticeably with the increase in inhibitor concentration indicating, the increased inhibition efficiency. Generally, in acidic solution the anodic process of corrosion is the passage of metal ions from the solid metal to the solution, and the principal cathodic process is the discharge of hydrogen ions to produce hydrogen molecules or reduction of oxygen. In the present study, the corrosion potential values are slightly shifted to more positive direction indicating that, addition of the inhibitor molecule reduces both anodic dissolution and cathodic reduction; therefore, Cephradine could be classified as a mixed type inhibitor with predominantly control of anodic reaction.

Surface Analysis

EDX examinations of the electrode surface

EDX survey spectra were used to determine which elements were present on the electrode surface before and after exposure to the inhibitor solution. Fig. 6 presents an EDX panorama recorded for LCS samples exposed to 1.0M HCl solution in the absence and presence of optimum concentration (15×10^{-4} M) of cephradin. In uninhibited HCl solution, the EDX spectra (Fig. 6a) confirm the existence of iron oxide and iron chloride, as indicated by the Fe, O and Cl signals. Also, the spectra show some constituents of carbon steel (C and Si signals). However, the EDX spectra of inhibited solution (Fig. 6b), showes enhancement of the C and O signals and also, additional line characteristic of sulphur is detected .This is due to carbon, oxygen and sulphur atoms present in cephradin molecule. These data confirm that an organic material containing carbon, oxygen and sulphur atoms has covered the electrode surface, this layer is undoubtedly due to the inhibitor. The weight percent of the elements present on carbon steel surface exposed to uninhibited and inhibited HCl solutions are presented in Fig. 7.The figure shows that the Fe peaks are considerably suppressed relative to the sample immersed in free 1.0M HCl solution, the suppression of the Fe lines occurs because of the overlying inhibitor film. This suggestion was further confirmed by the noticeable increase in the weight percent of oxygen and sulphur elements, and the appearance of sulphur on the metal surface in presence of inhibitor. It is clear that, this high contribution is not present on the electrode surface exposed to uninhibited HCl solution. These results confirm those obtained from polarization measurements, which suggest that a surface film inhibited the metal dissolution and hence retarded the hydrogen evolution reaction.

SEM observations of the electrode surface

The formation of a protective surface film of inhibitor on the electrode surface was further confirmed by SEM observations of the electrode surface. Fig. 8a shows SEM micrograph of polished LCS surface. Fig. 8 b,c show an array of SEM images recorded for LCS samples exposed to uninhibited and inhibited HCl solutions. The morphology of specimen surface in Fig. 8b reveals that in the absence of cephradin, the surface is highly corroded with areas of localized corrosion as indicated in the image. However, in presence of the inhibitor (image c), the rate of corrosion is suppressed on addition of inhibitor. The electrode surface is almost free from corrosion due to the formation of an adsorbed film of the inhibitor on the electrode surface. The protective nature of this film is reflected in the inhibition efficiency measurements obtained from electrochemical method. Therefore, EDX and SEM examinations of the electrode surface support the results obtained from gravimetric and electrochemical methods that cephradinm is a good inhibitor for LCS in HCl.
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Mechanism of inhibition

In hydrochloric acid medium, the metal surface is negatively charged due to the specifically adsorbed chloride ions on the metal surface.

$$Fe + Cl^- \leftrightarrow (FeCl^-)_{ads} \qquad ...(10)$$

In acidic solution, the nitrogen atoms of the Cephradine molecule can be protonated easily, due to high electron density on it, leading to positively charged inhibitor species. The adsorption can occur via electrostatic interaction between positively charged inhibitor molecules and negatively charged metal surface[15,41] leading to physisorpton of the inhibitor molecules. Further, co-ordinate bond may be formed between unshared e- pairs of unprotonated nitrogen atom of the inhibitor and vacant d-orbitals of metal surface atoms. Additionally inhibitor molecule may be chemically adsorbed due to interaction of π electrons of the aromatic ring of the inhibitor with vacant d-orbitals of metal[34].

CONCLUSIONS

(1). Cephradine acts as a good inhibitor for the corrosion of carbon steel in 1.0 M HCl.

(2). The inhibition efficiency of Cephradine increases with the increase in concentration while, it decreases with temperature.

(3). The adsorption of Cephradine obeys Langmuir adsorption isotherm. The adsorption process is a spontaneous and exothermic process accompanied by an increase of entropy.

(4). Potentiodynamic polarization curves reveals that Cephradine is a mixed-type but predominantly cathodic inhibitor.

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