

Electrochemical Studies of Ampicillin as Corrosion Inhibitor for Stainless Steel in Hydrochloric Acid Solution

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Abstract

The effect of Ampicillin (AMP) molecule on the corrosion resistance of stainless steel (SS) is studied using weight loss, open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy in 0.5 mol L⁻¹ HCl solution. The results obtained by weight loss measurements showed that the corrosion rate of the SS decreased fifty times in the presence of 10⁻³ M AMP. These results were in good agreement with those obtained by the potentiodynamic polarization and by the electrochemical impedance spectroscopy. Maximum inhibition efficiency of about 80% was found with 10⁻³ M AMP irrespective of the method being used. Potentiodynamic polarization measurements showed that the AMP is mixed-type inhibitor. The values of the thermodynamic parameters, such as adsorption equilibrium constant K_{ads} and standard free energy of adsorption ΔG_{ads} , were determined and discussed. These results showed that Ampicillin is a good inhibitor for stainless steel in 0.5 mol L⁻¹ HCl. The inhibition efficiency was found to increase with concentration of the inhibitor. The adsorption of Ampicillin on the stainless steel was found to spontaneous and fitted the Langmuir adsorption model.

Keywords: *Stainless steel; Corrosion; Inhibition; Ampicillin; Adsorption.*

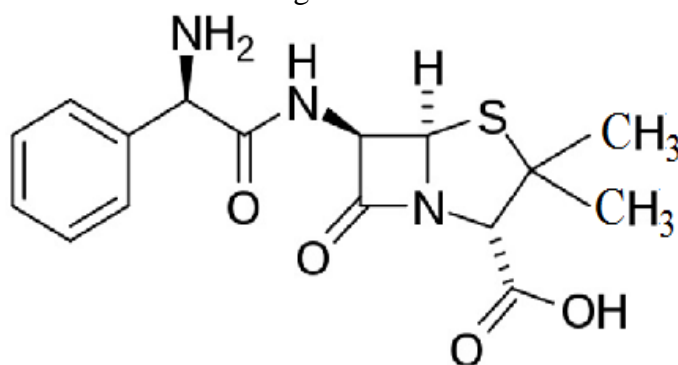
1. Introduction

Corrosion is a primary means by which metals deteriorate and is therefore a major industrial problem. The use of corrosion inhibitors is one of the most common methods used to protect metals against corrosion, in particular in acidic medium [1, 2]. Acids are widely used in industries such as pickling, cleaning, descaling, etc. Most inhibitors are organic compounds containing heteroatoms such as sulfur, nitrogen and oxygen or containing π -bonds [3-5]. Recently, research activities are geared towards developing cheap, non-toxic and environment friendly corrosion inhibitors [6]. Inhibitors decrease the corrosion rate by adsorbing on the metal surface and blocking the active sites by displacing water molecules and form a compact barrier film on the metal surface.

Antibacterial drug molecules generally containing heteroatom or/and multiple-bonds have been investigated as green corrosion inhibitors [7-18]. The results obtained from such studies have given

some hope for their use to protect various metals from corrosion. Recently, a review provided the state of the art on drugs used as corrosion inhibitors of different metals in various environments [13]. The Ampicillin molecule was already used as corrosion inhibitor in acidic media. According to Abdallah [14] effective corrosion inhibition of aluminum is possible in the presence of antibacterial drugs namely Ampicillin (AMP) in 2 mol L^{-1} HCl solution. The inhibitive action of AMP was attributed to blocking of the electrode surface by adsorption of the molecule through the active centers contained in their structure. Eddy et al. [15] studied the corrosion inhibition of AMP and its synergic combination with halides (KI, KCl and KBr) for the corrosion of mild steel in H_2SO_4 solution. It was found that the corrosion efficiencies of AMP for the mild steel increased with increasing the concentration of inhibitor but decreased with increasing the temperature. Corrosion inhibition potentials of AMP were also studied for mild steel in 0.1 mol L^{-1} HCl solution using gravimetric and Fourier transform infrared spectroscopy methods for monitoring corrosion [16]. Theoretical attempts to establish correlations between inhibition efficiencies and the electronic properties of some antibiotic molecules using different quantum chemical methods were investigated [7, 17, 18].

The present work describes a study of corrosion protection action of Ampicillin on stainless steel in 0.5 mol L^{-1} HCl using weight loss measurement and electrochemical techniques. Ampicillin (6-[2-amino-2-phenylacetamide] penicillanic acid), **Scheme 1**, is in the semi-synthetic penicillin that was first used in therapy [19]. The molecule is big enough (Molecular Mass: $349.40 \text{ g mol}^{-1}$) and sufficiently planar to block more surface area (due to adsorption) on stainless steel. These factors favor the interaction of AMP with the metal surface. As far as we know no concrete report has been published for stainless steel corrosion inhibition by AMP. The structure of the AMP is shown in the **Scheme 1**. Various concentrations of inhibitor were prepared and their corrosion inhibition efficiency on stainless steel in 0.5 mol L^{-1} HCl was investigated.



Scheme 1. Structure of ampicillin

2. Materials and methods

2.1. Material

316 stainless steel (SS) specimens of composition (wt%): C (0.03), Si (0.41), Cr (17.55), Mn (1.57), Ni (10.6), Mo (2.0) and Fe (balance), were used for electrochemical studies. Samples with sizes of $1 \text{ cm} \times 1 \text{ cm} \times 0.1 \text{ cm}$ cut in SS sheet were prepared by grinding each side with 1200 grid emery paper and degreasing the surfaces ultrasonically with ethanol and finally dried in open air. All reagents used for the study were of analar grade and the solutions were prepared using double distilled water.

2.2. Inhibitor

Ampicillin, with chemical formula, $C_{16}H_{19}N_3O_4S$, (Ampicillin sodium salt trihydrate powder used for cell culture media) was purchased from Sigma and used without further purification. Solutions of 0.5 mol L^{-1} HCl without inhibitor and with inhibitor whose concentration ranged from $10^{-5} \text{ mol L}^{-1}$ to 10^{-3} M were used.

2.3. Gravimetric Method

For weight loss measurements, pre-cleaned specimens were dipped in 100 mL of 0.5 mol L^{-1} HCl with and without the inhibitor maintained in a thermostated BOD chamber at $25 \pm 0.5^\circ\text{C}$. Weight loss measurement was determined by retrieving the coupons after 7 days of immersion. Triplicate specimens were used and the mean weight losses were reported. The difference in weight was taken as the weight loss of steel.

2.4. Electrochemical Measurements

Electrochemical studies were carried out in a three-electrode with single-compartment glass cell. The potential of the working electrode was measured against a saturated calomel electrode (SCE) (0.240 V vs. SHE). The SCE was connected through a KCl-containing agar-agar salt bridge, the tip was placed as close as possible to the surface of the working electrode in order to minimize the solution resistance between the working and the reference electrodes. The counter electrode was a platinum plate of 6 cm^2 surface. The aerated and unstirred electrolyte is used with the volume a 100 mL.

The electrochemical study was performed using a computerized electrochemical potentiostat (Votalab PRZ 100, Radiometer-Analytical). The corrosion behaviour of the SS was investigated using potentiodynamic polarization technique. The polarization curves were measured after determination of open circuit potential of the working electrode. For all electrochemical investigation, the open-circuit potential (OCP) was measured for 30 min. The polarization curves were recorded by sweeping the potential between -0.800 V and -0.150 V vs. SCE in 0.5 mol L^{-1} HCl solutions containing different concentrations of the tested inhibitor at a scan rate of 1 mV s^{-1} . The linear Tafel segment of the cathodic curves was extrapolated to E_{corr} to obtain corrosion current densities.

The experimental procedures and conditions employed in the electrochemical impedance spectroscopy, (EIS), study were similar to those described previously [20, 21]. The working electrode was immersed in the test solution for 30 minutes to reach a steady state open circuit potential. EIS measurements were carried out at open circuit potential within the frequency range of 10^{-2} - 10^5 Hz . An AC voltage amplitude of 10 mV peak-to-peak voltage excitation were employed. The results were displayed in the form of Nyquist plots. Each experiment was repeated at least three times to check the reproducibility.

3. Results and Discussions

3.1. Weight Loss Studies

The effect of addition of $10^{-3} \text{ mol L}^{-1}$ Ampicillin on the corrosion of stainless steel in 0.5 mol L^{-1} HCl was studied by weight loss method at 25°C after 7 days of immersion period. The inhibition efficiency of the inhibitor, E%, the degree of surface coverage, θ , and the corrosion rate (CR in $\text{g cm}^{-2} \text{ day}^{-1}$) of the steel were calculated using the following equations respectively:

$$CR = \frac{W}{At} \quad (1)$$

$$\theta = 1 - \frac{W}{W_0} \quad (2)$$

$$Ew = \left(1 - \frac{W}{W_0}\right) \times 100 \quad (3)$$

where W_0 and W are the weight losses (in g) for stainless steel in the absence and the presence of the inhibitor in 0.5 mol L⁻¹ HCl solution respectively, θ is the degree of surface coverage, A is the area of the SS coupon (in cm²) and t is the time of immersion (in days).

Table 1. Weight loss, surface coverage, θ , corrosion rate, CR, and Inhibition efficiency, Ew , of stainless steel obtained by weight loss method at 25 °C.

Inhibitor concentration (mol L ⁻¹)	Weight loss (g cm ⁻²)	Surface coverage θ	10 ⁴ x Corrosion rate (CR) in (g cm ⁻² day ⁻¹)	Inhibition efficiency Ew
0	0.0206	-	29.4	-
1x10 ⁻⁵	0.0164	0.20	23.4	20
5x10 ⁻⁵	0.0109	0.47	15.6	47
1x10 ⁻⁴	0.0073	0.65	10.4	65
5x10 ⁻⁴	0.0055	0.74	7.9	74
1x10 ⁻³	0.0041	0.80	5.9	80

The values of corrosion rate (CR), degree of surface coverage of the inhibitor (θ), and inhibition efficiency, (Ew) are shown in the **Table 1** for various concentration of the inhibitor. It is clearly seen, from data given in Table 1, that the presence of the inhibitor reduced the corrosion rate of steel in 0.5 mol L⁻¹ HCl solutions. Indeed, the inhibitory effect increased with the increase of the inhibitor concentrations. The decrease in corrosion rate with the addition of AMP is due to a protective effect of the inhibitor. The corrosion rate of the SS decreased fifty times in the presence of 10⁻³ M AMP in HCl solution. The corrosion inhibition efficiency, Ew , increased with the increase of inhibitor concentration. The inhibition efficiency, Ew , reached a maximum of 80% at 10⁻³ M AMP.

3.2. Open Circuit Potential

Figure 1 shows the open circuit potential (OCP) of the stainless steel electrodes versus time in aerated quiescent 0.5 mol L⁻¹ HCl solutions containing various concentration of AMP. At the onset of immersion, the OCP decreased steadily due to the aggressive chloride ions attack. Then the steady state reached at -0.67 V, -0.450 V and -0.430 V for the blank, 10⁻⁵ mol L⁻¹ and 10⁻⁴ mol L⁻¹ AMP respectively. The steady state might be due to the invariability of the interface composition. At higher concentration of AMP, i.e. 10⁻³ mol L⁻¹, the steady state is reached at -0.420 V in about 10 min after which the OCP shifts to noble potential value. OCP values obtained at the steady state, for the stainless steel, increased with increasing the AMP concentration. The ennoblement of OCP with increasing AMP concentration should predict good corrosion resistance of the steel. This increase of OCP suggests reduction of susceptibility of the alloy to corrosion process but OCP values do not provide any information on the corrosion kinetics [22]. That is to say that the steel interface immersed in 0.5

mol L⁻¹ HCl solution probably undergoes formation of oxides which may protect the metal and where adsorbed Cl⁻ ions react by pitting corrosion.

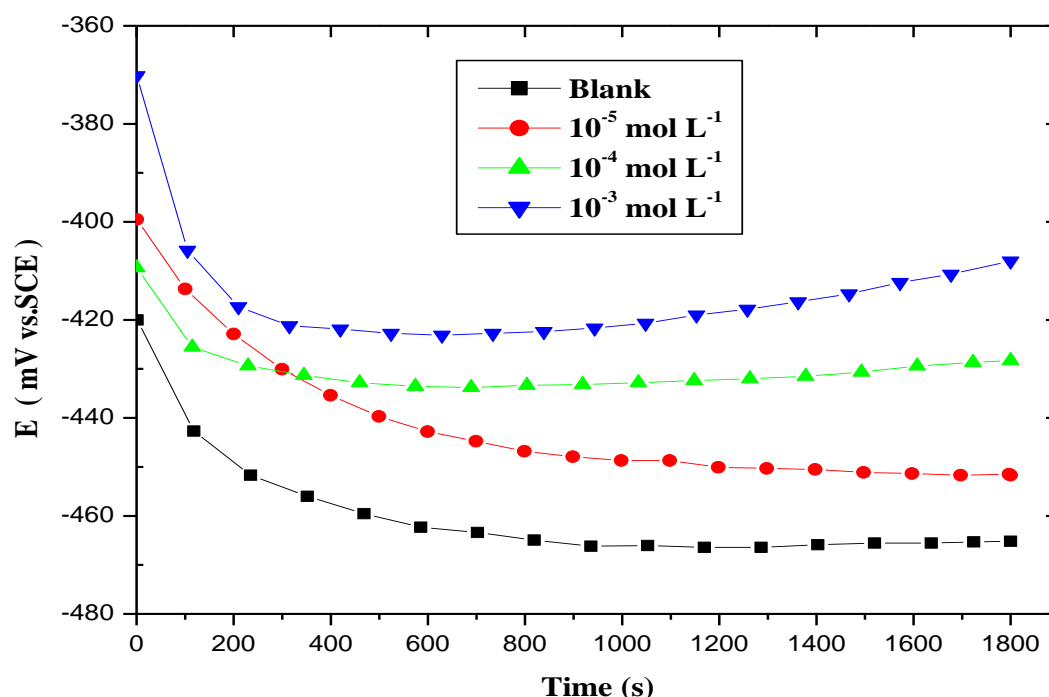


Figure 1. OCP curves for stainless steel electrode in 0.5 mol L⁻¹ HCl solution with and without various AMP concentrations.

3.2. Potentiodynamic Polarization

The electrochemical behaviour of stainless steel sample in inhibited and uninhibited solution are presented in **Figure 2** and listed in **Table 2**. Measurements were performed in the 0.5 mol L⁻¹ HCl solution containing various concentrations of AMP at a scan rate of 1 mV s⁻¹. All the polarization curves present the same trend. The cathodic polarization curves are assumed to represent the hydrogen evolution following Tafel behavior, while the anodic polarization curves represent the dissolution of stainless steel. The polarization curves obtained are similar to each other in terms of cathodic current densities. Thus, the hydrogen evolution is similar on the stainless steel at various AMP concentrations in 0.5 mol L⁻¹ HCl. The cathodic curves indicated that the cathodic process was not diffusion controlled. Therefore the slope of the cathodic curves was steep. Addition of the AMP to acid media reduced the anodic current densities and shifted corrosion potentials, E_{corr} , in the positive direction. The linear Tafel segments of cathodic part were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}).

Due to the occurrence of the passivation on the anodic branch of the potentiodynamic polarization curves, the potential range for the linear Tafel behaviour was very short making it difficult to accurately determine the corresponding Tafel slope [23-25]. The curvature of the anodic branch may be attributed to the deposition of the corrosion products on the steel surface [25]. According to Amin and Ibrahim [26], and Bockris and Reddy [27], extrapolation of the cathodic branch would be

sufficient to compute the corrosion current by Tafel extrapolation to corrosion potential. They [26, 27] argued that concentration effect due to passivation and dissolution may be the cause of the deviation from Tafel behaviour on the anodic branch. Thus, extrapolation of the cathodic Tafel region back to zero overvoltage would give the net rate of the cathodic reaction at the corrosion potential. This is also the net rate of the anodic reaction at the corrosion potential which verified by other non-electrochemical techniques [28].

For inhibited system, if the displacement in E_{corr} value is greater than 85 mV relative to uninhibited system then the inhibitor is classified as cathodic or anodic type [7]. In this work, the maximum displacement of E_{corr} value is only 64 mV, hence the Ampicillin was classified as a mixed-type inhibitor.

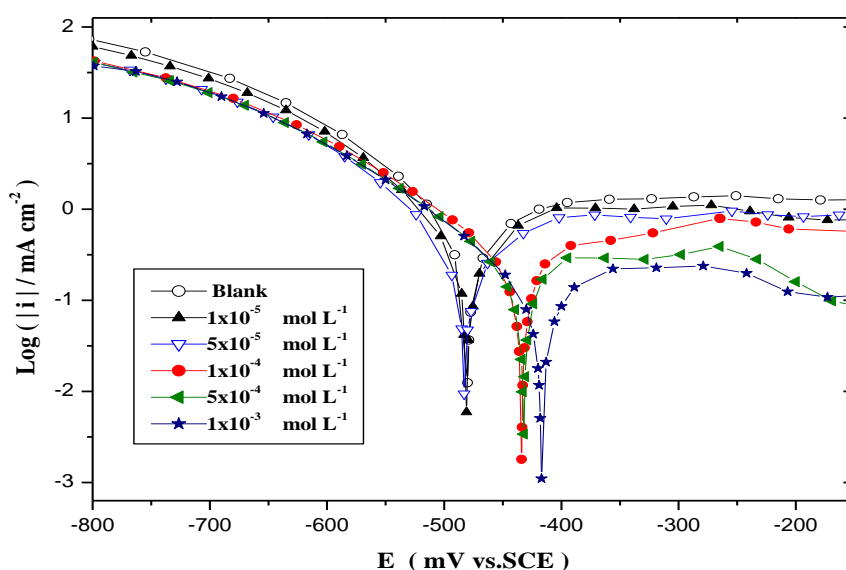


Figure 2. Tafel polarization curves for corrosion of stainless steel in 0.5 mol L⁻¹ HCl in the absence and presence of various concentrations of Ampicillin, $\nu = 1 \text{ mV s}^{-1}$.

Table 2. Calculated electrochemical parameters for SS in the absence and presence of various concentrations of AMP in 0.5 mol L⁻¹ HCl.

C_{inh} (mol L ⁻¹)	E_{corr} (V vs. SCE)	I_{corr} (mA cm ⁻²)	$-\beta_c$ (V dec ⁻¹)	Ep%
Blank	-0.480	0.74	0.116	-
10^{-5}	-0.479	0.58	0.116	22
5×10^{-5}	-0.479	0.37	0.112	50
10^{-4}	-0.435	0.23	0.112	69
5×10^{-4}	-0.434	0.17	0.112	78
10^{-3}	-0.416	0.12	0.112	84

The electrochemical parameters obtained from polarization curves including open circuit potential, corrosion potential (E_{corr}), and corrosion current densities (I_{corr}), the cathodic Tafel slopes (β_c) and the inhibition efficiencies, are summarized in **Table 2**. Judging from the polarization curves **Figure 2** the anodic current densities are obviously lowered as a result of the addition of various concentration of

inhibitor. The corrosion current densities **Table 2**, decreased as the Ampicillin concentration increased in the acidic solution. Tafel slopes of the cathodic curves were approximately the same. The inhibition efficiency $E_p\%$ was evaluated from the measured I_{corr} values using the relationship? where, I_{corr}^0 and I_{corr} are the corrosion current density in the absence and presence of inhibitor, respectively:

$$E_p\% = \frac{(I_{corr}^0 - I_{corr})}{I_{corr}^0} \quad (4)$$

The inhibition efficiency values, **Table 2**, showed that the Ampicillin acted as very effective corrosion inhibitor for stainless steel in 0.5 mol L^{-1} HCl solution and its capacity of inhibition increased with increase of its concentration. The maximum inhibition efficiency, 84%, was obtained at a concentration of $10^{-3} \text{ mol L}^{-1}$ AMP. These results are consistent with the results obtained by OCP measurements.

3.3. Electrochemical Impedance Spectroscopy

Electrochemical impedance measurements were carried out over the frequency ranging from 100 kHz to 0.01 Hz at open circuit potential. Nyquist plots for stainless steel corrosion in 0.5 mol L^{-1} HCl in the absence and the presence of various concentrations of AMP are given in **Figure 3**. The inhibition efficiency, $EI\%$, was evaluated from the measured charge transfer resistance values obtained from Nyquist plots using the relationship:

$$EI\% = \frac{(R_{ct} - R_{ct}^0)}{R_{ct}} \quad (5)$$

where R_{ct}^0 and R_{ct} are the charge transfer resistance in absence and presence of inhibitor, respectively. The deduced parameters such as charge transfer Resistance (R_{ct}), inhibition efficiencies ($EI\%$) and the surface coverage (θ), (where $\theta = E\%/100$) of stainless steel in 0.5 mol L^{-1} HCl containing various concentrations of Ampicillin are presented in **Table 3**.

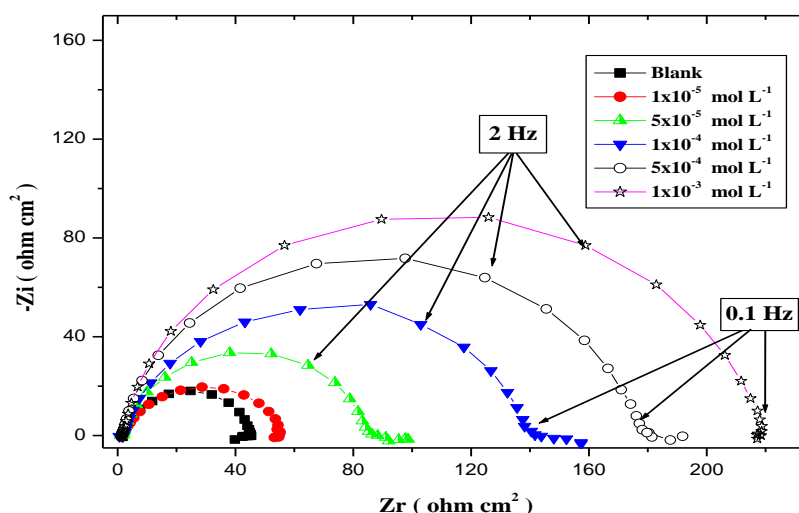


Figure 3. Nyquist plots of stainless steel in 0.5 mol L^{-1} HCl in the absence and presence of various concentrations of AMP.

Table 3: electrochemical parameters such as charge transfer resistance (R_{ct}) inhibition efficiencies (EI%) and the surface coverage (θ), (where $\theta = \text{EI\%}/100$) of stainless steel in 0.5 mol L^{-1} HCl without and with the addition of various concentrations of AMP.

Concentration (mol L^{-1})	Charge transfer resistance R_{ct} (ohm cm^2)	Surface coverage θ	Inhibition efficiency EI%
Blank	45	-	-
1×10^{-5}	55	0.18	18
5×10^{-5}	85	0.47	47
1×10^{-4}	140	0.68	68
5×10^{-4}	178	0.75	75
1×10^{-3}	218	0.80	80

Figure 3 and **Table 3** showed clearly that the impedance of the inhibited stainless steel increased with the increase of the inhibitor concentration. The increased diameter of Nyquist plot in 0.5 mol L^{-1} HCl in the presence of AMP indicated the corrosion inhibition of stainless steel. A depressed semicircle is mostly referred to as frequency dispersion which could be attributed to different physical phenomena such as roughness and inhomogeneities of the solid surfaces, impurities, grain boundaries and distribution of the surface active sites [29].

A small inductive loop can be seen in Nyquist plot 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 $(\text{Cl}^-)_{\text{ads}}$ on the electrode surface. This may also be attributed to the re-dissolution of passivated surface [30].

It is worth noting that the percentage inhibition efficiencies obtained from impedance measurements are comparable and run parallel with those obtained from potentiodynamic polarization and weight loss measurements.

3.4. Adsorption Consideration

The primary step in the action of inhibitors in acid solutions is their adsorption onto the metal surface, which is usually oxide-free. The adsorbed inhibitor then acts to retard the cathodic and/or anodic electrochemical corrosion reaction. Basic information on the interaction between the inhibitor and the stainless steel surface can be provided by the adsorption isotherm. In this study, Langmuir adsorption isotherm was found best for describing the adsorption behaviour of Ampicillin on the stainless steel surface in 0.5 mol L^{-1} HCl solution. Langmuir adsorption isotherm is described by the following equation:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (6)$$

Where K_{ads} is the equilibrium constant of the adsorption process, θ is surface coverage and C_{inh} is the inhibitor concentration.

The dependence of the fraction C_{inh} / θ as a function of C_{inh} of AMP is shown **Figure 4**. The obtained plots of the inhibitor are almost linear with a correlation coefficient 0.999.

The equilibrium constant of adsorption K_{ads} is related to the standard free energy of adsorption ΔG_{ads} , by the following equation:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^0}{RT}\right) \quad (7)$$

where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution expressed in M.

Generally, values of ΔG_{ads}^0 around -20 KJ mol^{-1} or less negative are consistent with electrostatic interaction (physisorption) while those -40 KJ mol^{-1} and more negative involve electron transfer to form chemical bond (chemisorptions) [31, 32].

The value of the equilibrium constant obtained, in the present work, from the Langmuir isotherm is $K_{abs} = 25000 \text{ L mol}^{-1}$. The high value of K_{ads} for studied inhibitor indicates stronger adsorption on the steel surface in 0.5 M HCl solution. The calculated value of ΔG_{ads}^0 was $-34.5 \text{ KJ mol}^{-1}$ which is consistent with the spontaneity of the adsorption process of AMP and the stability of the adsorbed layer on the steel surface. The later value is negatively less than the threshold value of -40 KJ mol^{-1} which is required for chemical adsorption. The value of ΔG_{ads} calculated in this work indicates that the adsorption of AMP is not merely physisorption nor chemisorption. Therefore, this value of ΔG_{ads}^0 confirms that the adsorption of AMP is not a simple physisorption but it may involve some other interactions [33, 34].

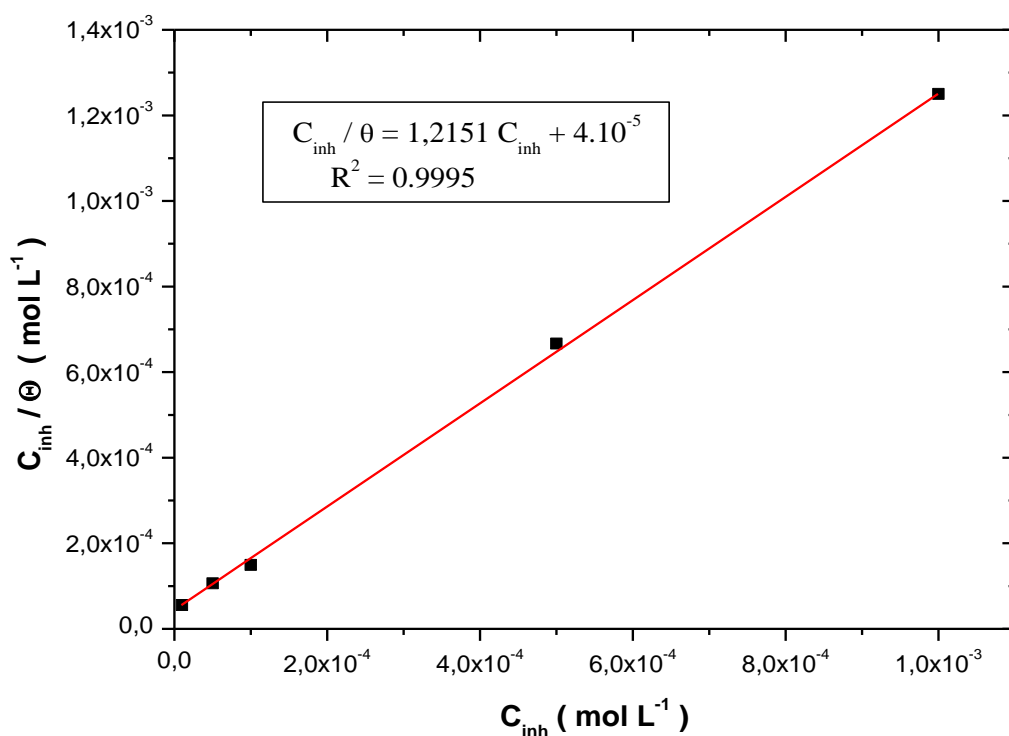


Figure 4. Langmuir isotherm for the adsorption of AMP on SS surface.

Thus, the mechanism of corrosion inhibition of steel in acidic solution by AMP could be explained on the basis of adsorption on the metal surface. According to Golestani et al. [32], AMP molecules exist in acidic solutions either in neutral or protonated molecules ($-\text{NH}_3^+$ groups) which may involve

adsorption and displacement of water molecules from the steel surface. Physisorption originates from electrostatic interactions of charged molecules with positively charged surface steel while chemisorption involves donor–acceptor interactions between π electrons of aromatic molecules and free electron pairs of heteroatoms (N, S, and O) and vacant d-orbitals of Fe atoms to form coordinate type bond [35].

Chloride ions adsorbed on positively charged steel surface constitute a bridge between the metal surface and protonated inhibitor molecules [36]. Therefore, considering the chemical structure of AMP, physisorption and chemisorption adsorption or mixed mode of adsorption may occur. According to Eddy et al. [15] and Golistani et al. [32] AMP adsorbs on steel following Physical adsorption mechanism in acidic media.

This point merits to be deeply investigated in future to discriminate between physisorption and chemisorption pathway of AMP on the surface steel in acidic media.

Conclusion

Ampicillin was found to be a good adsorption inhibitor for the corrosion of stainless steel in 0.5 mol L⁻¹ HCl. The results obtained from weight loss run parallel with those obtained from potentiodynamic polarization and IES measurements. Potentiodynamic polarization measurements showed that AMP is a mixed-type inhibitor. The values of the equilibrium constant and the standard free energy of adsorption obtained from the Langmuir isotherm were $K_{\text{ads}} = 25000 \text{ L mol}^{-1}$ and $\Delta G_{\text{ads}} = -34.5 \text{ KJ mol}^{-1}$ respectively. The adsorption was found to be spontaneous and fitted the Langmuir adsorption model.

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