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THE INFLUENCE OF AMPICILLIN ON THE CORROSION INHIBITION OF MILD STEEL IN IN HYDROCHLORIC ACID SOLUTION

S. HariKumar, S. Karthikeyan

Materials Chemistry Division, School of Advanced Sciences, VIT University, Vellore

E-mail of Corresponding Author: skarthikeyanphd@yahoo.co.in

ABSTRACT

The effect of an antibiotic ampicillin is studied for use as a low cost and ecofriendly corrosion inhibitor for mild steel in acidic environment. The corrosion inhibition effect is investigated using weight loss, Tafel polarization, electrochemical impedance spectroscopy and hydrogen permeation studies. The inhibitor showed 80% inhibition efficiency at $15 \times 10^{-4} \text{M}$ concentration of ampicillin. Potentiodynamic polarization suggests that it is a mixed type of inhibitor. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition. Hydrogen permeation measurements indicated that the compound behave as cathodic inhibitor, but predominantly under mixed control. Diffused reflectance spectroscopy (DRS) studies confirmed only the mere adsorption of Ampicillin on mild steel surface and not influence on the surface morphology. The adsorption of this compound on mild steel surface obeys Temkin's adsorption isotherm.

Keywords: Corrosion test, electrochemical techniques, adsorption

1. INTRODUCTION

Mild steel is an important category of materials due to their wide range of industrial applications. It is used in many industries due to its excellent mechanical properties. These are used in industries as pipelines for petroleum industries, storage tanks, reaction vessels and chemical batteries(1). Acids are widely used for Pickling, Descaling, Acid Cleaning, Oil Well acidizing and other applications. Due to their high corrosive nature acids may cause damage to the system components. Various methods are used to decrease the corrosion rate of metals in acids, among the different methods use of inhibitors is most commonly used (2-7). The use of corrosion inhibitors is most economical and practical method to reduce electrochemical corrosion. Heterocyclic compounds containing heteroatoms such as S,

N & O act as effective corrosion inhibitors for mild steel in acid media and have been the subject of many publications(8-11).

Organic compounds have been widely used as corrosion inhibitors for metals in acidic media(12-18). The effective and efficient corrosion inhibitors were those compounds which have π bonds and contains hetero atoms such as sulphur, nitrogen, oxygen and phosphorous which allows the adsorption of compounds on the metal surface(19-23). The organic 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. The most of the organic inhibitors are toxic, highly expensive and environment unfriendly. Research activities in recent times are geared towards developing the cheap, non-toxic and environment friendly corrosion inhibitors.

The present paper describes a study of corrosion protection action of Ampicillin on mild steel in 1N HCl using weight loss, electrochemical techniques and hydrogen permeation studies. Ampicillin is a antibiotic with π -electrons, heteroatoms S, N & O. The molecule is big enough (Molecular Mass-403.45) and sufficiently planar to block more surface area (due to adsorption) of mild steel. These factors favour the interaction of ampicillin with the metal. As far as we know no concrete report has been published so for Ampicillin in 1N HCl with use of electrochemical techniques ,hydrogen permeation and diffuse reflectance spectra. Hence the present study. The structure of the ampicillin is shown in the fig.1. Different concentrations of inhibitor were prepared and there inhibition efficiency in acidic media was investigated.

2. EXPERIMENTAL SECTION;

2.1. Materials and Methods;

Mild steel specimens of size 1x4 cm² were used for weight loss and electrochemical studies. The surface of each specimen was abraded with different emery papers and washed with acetone. The cleaned samples were then washed with double distilled water and finally dried. Electrochemical experiments were performed using a three electrode cell assembly with mild steel samples as working electrode, platinum as counter electrode and saturated calomel (SCE) as the reference electrode. AR grade Hydrochloric Acid and doubly distilled water were used to prepare 1N acid for all experiments.

2.2. Inhibitor;

Ampicillin was purchased from medicine shop as a trade name Ampicillin capsules (Biocilin capsules) and used without further purification. Ampicillin is a N-S heterocyclic compound containing four oxygen atoms, three nitrogen atoms and one sulphur atom. Hence it is expected to act as a good inhibitor. The range of the concentrations of inhibitor used for the inhibiton is from 5×10^{-4} to 15×10^{-4} .

2.3. Mass Loss Studies;

Different mild steel samples were immersed in hanging positions in 1N HCl solution containing different concentrations of inhibitors for three hours. Samples were weighed before and after immersion and weight differences were determined. The degree of surface coverage (θ) and percentage inhibition efficiency (IE %) were calculated from the following equations

$$\text{Surface Coverage } (\theta) = W_0 - W / W_0$$

$$\text{Inhibition Efficiency (IE \%)} = (W_0 - W / W_0) \times 100$$

Where W_0 and W are the weight losses of mild steel without and with the inhibitor respectively. It was assumed that the surface was saturated with adsorbed inhibitor molecules, that is $\theta = 1$.

2.4. Tafel Polarization Studies;

Electrochemical measurements were carried out in a conventional three - electrode cylindrical glass cell, using CH electrochemical analyzer. Before recording the polarization curves the solution was deaerated for 20 min. and the working electrode was maintained at its corrosion potential for 10 min. until a steady state was obtained. The mild steel surface was exposed to various concentrations of ampicillin in 100mL of 1N HCl at room temperature. The inhibition efficiency (IE%) was calculated using the equation

$$\text{Inhibition Efficiency (IE \%)} = (I_0 - I / I_0) \times 100$$

Where I_0 and I are the corrosion current density without and with the inhibitor respectively.

The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -750mV to +150mV versus the open circuit potential. The corresponding corrosion current (I_{corr}) was recorded. Tafel plots were constructed by plotting E versus $\log I$. Corrosion Potential (E_{corr}), corrosion current density (I_{corr}) and

cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures.

2.5. Electrochemical Impedance Spectroscopy;

Impedance measurements were carried out in the frequency range from 0.1 to 10000 Hz using an amplitude of 20 mV and 10 mV peak to peak with an AC signal at the open-circuit potential. The impedance diagrams were plotted in the nyquist representation. Charge transfer resistance (R_{ct}) values were obtained by subtracting the high-frequency impedance. The percentage inhibition efficiency was calculated from the equation

$$\text{Inhibition Efficiency (IE\%)} = (R_{ct} - R'_{ct} / R_{ct}) \times 100$$

Where R'_{ct} and R_{ct} are the corrosion current of mild steel with and without inhibitor respectively.

2.6 Hydrogen permeation studies

The hydrogen permeation study was carried out using an adaptation of modified Devanathan and Stachurski's, two compartment cell. Hydrogen permeation current were obtained in the absence and presence of ampicillin used in the present study.

3. RESULTS AND DISCUSSION

3.1. Mass loss studies;

The values of inhibition efficiency (IE%) and the corrosion rate (CR) obtained from weight loss method at different concentrations of ampicillin are summarized in table-1. It follows from the data that the weight decreased and therefore corrosion inhibition increased with increase in inhibitor concentration. It was also observed that corrosion rate decreased with increase in inhibitor concentration.

It is evident from the table that ampicillin inhibits the corrosion of mild steel in HCl solution at all the concentrations used in the study i.e. 5×10^{-4} to 15×10^{-4} . Maximum inhibition efficiency was obtained at the concentration 5×10^{-4} . The increased inhibition efficiency and decreased corrosion rate might

be due to the increased adsorption and increased surface coverage (θ) of inhibitor on mild steel surface with increase in concentration.

3.2. Tafel Polarization;

Polarization curves for mild steel in 1N HCl at Various concentrations of ampicillin are shown in the **fig. 2**. The values of corrosion potential (E_{corr}), current densities (I_{corr}), anodic tafel slopes (β_a), cathodic tafel slopes (β_c), surface coverage(θ) and inhibition efficiency as a functions of ampicillin concentration were calculated from the curves are shown in table 2. It is evident from the figure that cathodic tafel slopes (β_c) remain almost unchanged with increasing inhibitor concentration. This indicates that hydrogen evolution is activation controlled and the addition of inhibitor did not change the mechanism of cathodic hydrogen evolution reaction (24,25).

It is observed that the inhibition efficiency increased with increasing ampicillin concentration and exhibited both cathodic and anodic inhibition through adsorption on the mild steel surface blocking active sites(26). There is no definite changes observed in the corrosion potential(E_{corr}). According to Riggs (27) and others if the displacement in E (i) is $>85\text{mV}$ with respect to E, the inhibitor can be seen as a cathodic or anodic type, (ii) if displacement in E is <85 , the inhibitor can be seen as mixed type. In our study the maximum displacement was 16mV , which indicates that ampicillin is a mixed type inhibitor.

It is evident from the data that inhibition efficiency (IE), surface coverage(θ) increases with increase in concentration of the inhibitor. The corrosion current density (I_{corr}) decreases with increase in inhibitor concentration. The maximum inhibition efficiency of 80.58% is obtained at $15 \times 10^{-4}\text{M}$ solution of ampicillin.

3.3. Electrochemical Impedance Spectroscopy (EIS) studies;

Corrosion inhibition of mild steel in 1N HCl solution with and without inhibitor was investigated by electrochemical impedance spectroscopy measurements and the results are

present in table 3.. The nyquist representations of impedance behavior of mild steel in 1N HCl with and without addition of different concentrations of ampicillin are shown in the **fig. 3**. It is observed from the fig. that at all concentration range of ampicillin one large capacitive loop at higher frequency range followed by the one small inductive loop at lower frequency range. The diameter of the circle increased with increase in inhibitor concentration. The higher frequency capacitive loop is due to the adsorption of inhibitor molecule(28).

This can be interpreted by R_s - R_p - C_{dl} equivalent circuit, commonly known as Randle circuit(fig.), which was previously used to model the iron-acid interface(29). Many workers also explained the results by using Randle circuit (29-34). The deviation from the perfect semi circle shape (depression) is often referred to the frequency dispersion of interfacial impedance. This behavior is due to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena (35-37).

It is observed that addition of inhibitor increases the values of R_{ct} and reduces the C_{dl} value. The decrease in C_{dl} is due to increase in thickness of the electronic double layer(38). The increase in R_{ct} values is due to the formation of protective film on the metal/solution interface(39,40). This observations suggests that ampicillin molecules function by adsorption on metal surface and thereby causing the decrease in C_{dl} values and increase in R_{ct} values.

4.Mechanism of corrosion inhibition;

Corrosion inhibition mechanism in acidic medium is based on the adsorption of inhibitor on the metal surface. The process of adsorption is influenced by the nature and charge of the metal,chemical structure of the inhibitor and the type of the aggressive electrolyte. The charge of the metal surface can be determined from the potential zero charge(pzc) on the correlative scale(ϕ_c)(41) by the equation

$$\Phi_c = E_{corr} - E_{q=0}$$

Where $E_{q=0}$ is the potential of zero charge. He value of E_{corr} obtained in HCl is -470mV versus SCE. In HCl solution Ampicillin acts as a protonated species. This protonated species are adsorbed on the metal surface through chloride bridge and reduces the corrosion.

Benerijee and Malhotra [42] reported the pzc of iron in hydrochloric acid solution is -530 mV versus SCE. Therefore the value of ϕ is +60 mV versus SCE, so the metal surface acquires slight positive charge. The adsorption of cationic Ampicillin species does not take place and the adsorption of chloride ions occur and surface becomes negatively charged. Now due to the electrostatic attraction, the protonated Ampicillin molecules are physically adsorbed on the metal surface and thereby giving high inhibition by Ampicillin molecules. Ampicillin molecules also adsorbed through their planar p-orbitals on the metal surface having vacant d- orbitals to inhibit the corrosion [43].

5. Adsorption Isotherm

The degree of Surface Coverage (θ) for different concentrations of inhibitor in 1N HCl has been calculated from weight loss, Polarization and Electrochemical Impedance studies. The obtained data was tested graphically for fitting suitable isotherm. Almost a straight line was obtained by plotting surface coverage (θ) Vs log C shown in Figure.4, which proves that the adsorption of this compound obeys Temkin isotherm.

6.Hydrogen Permeation Measurements

The variation of permeation current against time for mild steel in 1M HCl solution in the absence and presence of inhibitor is given in table 4.. The inhibitor brings down the permeation currents effectively. The order of the reduction in permeation current is same as the order of extent of corrosion inhibition. The reason for the best performance of inhibitor is due to enhance cathodic polarization to a

greater extent than anodic polarization. So it is found to enhance the energy barriers for the proton discharge which leads to less permeation of hydrogen through the mild steel. This experiment was carried out according to the procedure adopted by Devanathan and Stachurski two compartment cell (44).

7. UV Spectral Reflectance Studies

The surfaces of corroded and corrosion inhibited mild steel specimens were examined by diffuse reflectance studies in the region 200-700 nm using U-3400 spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan).

The corrosion inhibition of mild steel in 1N HCl in the presence of inhibitor may be due to the formation of thin film on the surface of the metal surface. This is supported by the reflectance studies carried out using spectrophotometer in different concentrations of inhibitor with different mild steel specimens. A reflectance curves for polished specimen, specimen dipped in blank solution and different concentrations of inhibitor is shown in the fig.5.

It can be seen from the curves that the percentage of reflectance is maximum for polished mild steel and it gradually decreases for the specimen dipped in 1N HCl solution. This observation reveals that the change in surface characteristic is due to the corrosion of mild steel. In the case of specimens immersed in acid containing different concentrations of ampicillin the reflectance percentage decreased only to small extent. This confirms that the surface characteristics are not altered more due to the formation of film on the surface. The reflectance percentage increased as the concentration of inhibitor increased due to the increase in thickness of the film formed.

7. CONCLUSION

- i) Ampicillin acts as a good inhibitor for the corrosion of mild steel in 1N HCl.
- ii) Potentiodynamic curves reveals that ampicillin is a mixed type of inhibitor.

- iii) The results obtained from weight loss, impedance and polarization studies are in good agreement with each other.
- iv) The adsorption of ampicillin on mild steel surface obeyed Temkin adsorption isotherm.
- v) The reduction in hydrogen permeation currents in the presence of inhibitors confirm the impressive performance of the compound.
- vi) DRS studies reveal that there is no significant changes in surface morphology as the compound merely adsorb on the mild steel surface.

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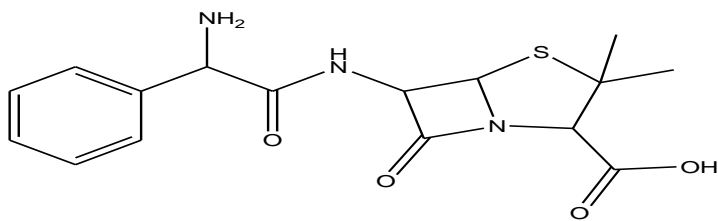


Figure 1. Structure of Ampicillin

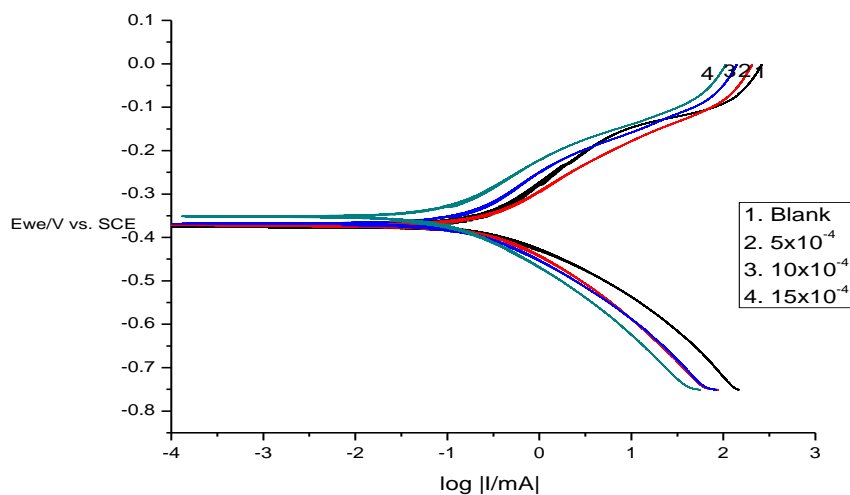


Figure 2. Potentiodynamic polarization curves for mild steel in 1N HCl with different concentrations of Ampicillin

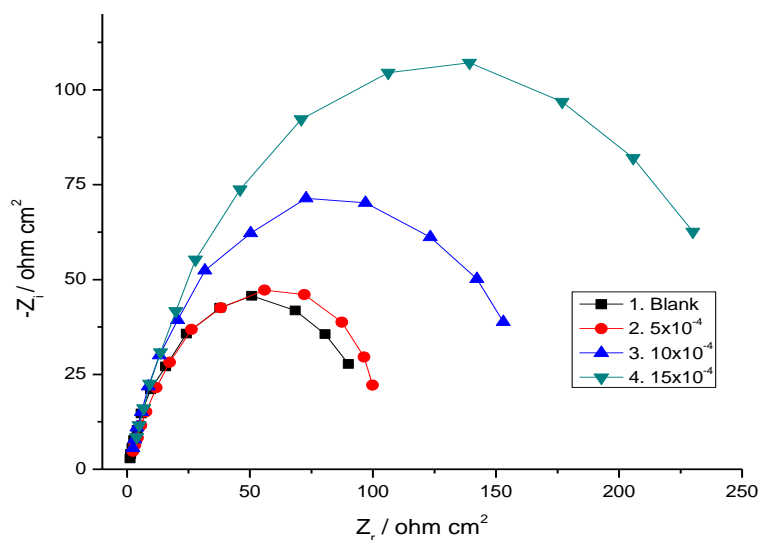


Figure 3: Nyquist plot of mild steel in 1N HCl with different concentrations of Ampicillin.

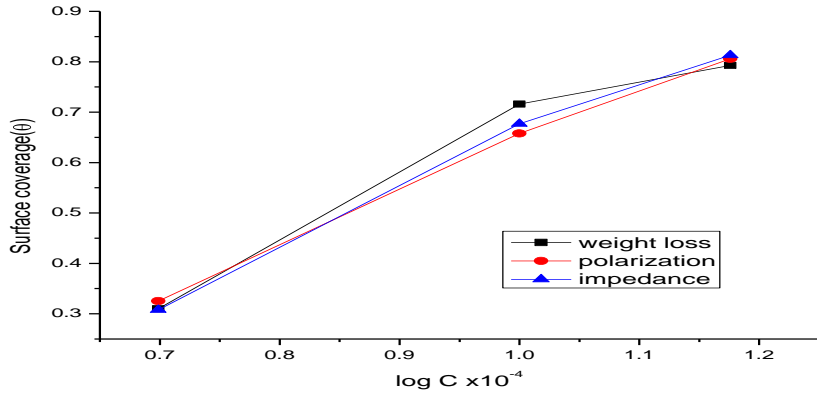


Fig. 4. Temkin Adsorption isotherm for different concentrations of Ampicillin in 1N HCl

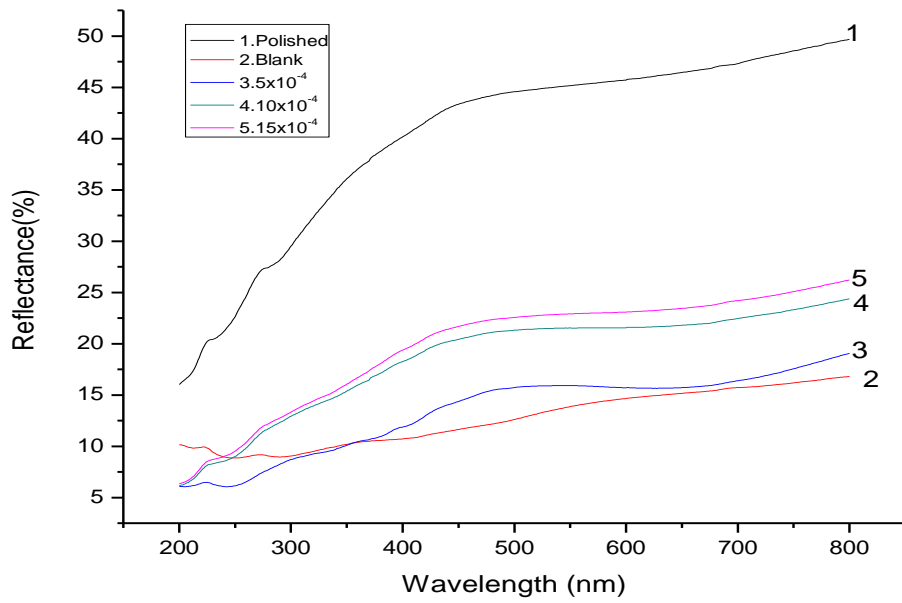


Figure 5. UV Reflectance curves for Mild Steel in 1N HCl solution with different concentrations of Ampicillin

Table 1. Values of Inhibition Efficiency, Corrosion rate and Surface coverage for the corrosion of mild steel in 1N HCl in presence of different concentrations of Ampicillin obtained from weight loss measurements.

Concentration (M)	Weight Loss (g)	Inhibition Efficiency (IE %)	Corrosion Rate ($\text{mgcm}^{-2}\text{h}^{-1}$)	Surface Coverage (θ)
Blank	0.0487	-	4.05	-
5×10^{-4}	0.0336	31.00	3.15	0.3100
10×10^{-4}	0.0138	71.60	1.15	0.7160
15×10^{-4}	0.0101	79.26	1.041	0.7926

Table 2: Electrochemical parameters and Inhibition Efficiency for corrosion of mild steel in 1N HCl obtained by Polarization method

Conc. (M)	E _{corr} (mV Vs SCE)	I _{corr} ($\mu\text{A cm}^{-2}$)	β_a (mV dec-1)	β_c (mV dec-1)	Surface Coverage (θ)	I.E. (%)
Blank	-355	412	144	125	-	-
5×10^{-4}	-354	278	114	147	0.3252	32.52
10×10^{-4}	-338	141	103	132	0.6577	65.77
15×10^{-4}	-326	80	94	136	0.8058	80.58

Table 3: Electrochemical parameters and Inhibition Efficiency for corrosion of mild steel in 1N HCl obtained by Impedance method.

Concentration (M)	R_{ct} (Ωcm^2)	C_{dl} (F cm^{-2})	surface coverage (θ)	Inhibition efficiency (%)
Blank	74	0.459	-	-
5×10^{-4}	107.6	0.290	0.308	30.84
10×10^{-4}	228.6	0.185	0.6768	67.68
15×10^{-4}	396.7	0.172	0.8130	81.30

Table – 4 .Values of hydrogen permeation current for the corrosion of mild steel in 1N HCl

Concentration of Inhibitor	%IE	Permeation current μA
Blank	--	18.5
5×10^{-4}	31.00	12.1500
10×10^{-4}	71.60	5.2125
15×10^{-4}	79.26	4.9875