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The influence of Co-Amoxiclav on the corrosion inhibition of mild steel in 1 N hydrochloric acid solution

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Abstract

The influence of an antibiotic Co-Amoxiclav is studied for use as a low cost and ecofriendly corrosion inhibitor for mild steel in acidic environment in particular to 1 N hydrochloric acid medium. The corrosion inhibition effect and the performance of the inhibitor has been extensively studied by weight loss studies, Tafel polarization experiments, electrochemical impedance spectroscopy and hydrogen permeation measurements. The dosage of the antibiotic was varied from 5×10^{-4} M to 15×10^{-4} M. It has been established that the inhibitor performed well and showed 88% inhibition efficiency at 15×10^{-4} M concentration of Co-Amoxiclav molecules. The electrochemical studies such as Potentiodynamic polarization proposes that the antibiotic *viz.*, Co-Amoxiclav acted as a mixed type of inhibitor. The increased charge transfer resistance and decreased double layer capacitance obtained from electrochemical impedance spectroscopy confirmed that said antibiotic has performed as good inhibitor in 1 N hydrochloric acid medium. Hydrogen permeation measurements showed that the compound acts as cathodic inhibitor, but predominantly under mixed control. It has been noticed that a definite correlation exists between chemical and electrochemical studies for the inhibition action of Co-Amoxiclav molecules on the corrosion of mild steel in 1 N HCl medium. Diffused reflectance spectroscopy (DRS) studies established that only the mere adsorption of antibiotic on mild steel surface took place and not influence on the surface morphology. The adsorption of this compound on mild steel surface obeys Temkin's adsorption isotherm.

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, and 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 discusses a study of corrosion protection action of Co-Amoxiclav on mild steel in 1 N HCl using weight loss, electrochemical techniques and hydrogen permeation studies. Co-Amoxiclav 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 Co-Amoxiclav with the metal. As far as we know no concrete report has been published so for Co-Amoxiclav in 1 N HCl with use of electrochemical techniques, hydrogen permeation and diffuse reflectance spectra. Hence the present study. The structure of the Co-Amoxiclav is shown in the Figure 1. Different concentrations of inhibitor were prepared and there inhibition efficiency in acidic media was investigated.
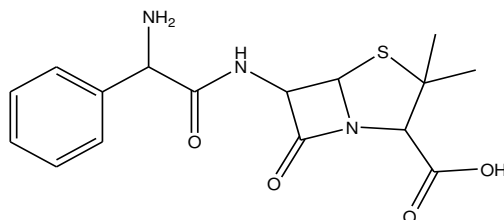
Figure 1. Structure of Co-Amoxiclav.

2. Experimental

2.1. Materials and Methods

Mild steel specimens of size 1×4 cm^2 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 1 N acid for all experiments.

2.2. Inhibitor

Co-Amoxiclav was purchased from medicine shop as a trade name Amaox-Clav capsules and used without further purification. Co-Amoxiclav is an 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 inhibition is from 5×10^{-4} M to 15×10^{-4} M.

2.3. Mass Loss Studies

Different mild steel samples were immersed in hanging positions in 1 N 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 cyclindrical 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 Co-Amoxiclav in 100 mL of 1 N 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 -750 mV to $+150$ mV *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 (βc and βa) 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 substracting 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 was obtained in the absence and presence of Co-Amoxiclav compound 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 Co-Amoxiclav 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 Co-Amoxiclav 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} M. Maximum inhibition efficiency was obtained at the concentration 5×10^{-4} M. 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.

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

Concentration (M)	Weight Loss (g)	Inhibition Efficiency (IE %)	Corrosion Rate (mg cm^{-2} h^{-1})	Surface Coverage (θ)
Blank	0.0487	–	4.05	–
5×10^{-4}	0.0312	38.00	3.11	0.3800
10×10^{-4}	0.0119	78.60	1.06	0.7860
15×10^{-4}	0.0010	88.2	1.001	0.8820

3.2. Tafel Polarization

Polarization curves for mild steel in 1 N HCl at Various concentrations of Co-Amoxiclav are shown in the Figure 2. The values of corrosion potential (E_{corr}), current densities (I_{corr}), anodic Tafel slopes (βa), cathodic Tafel slopes (βc), surface coverage (θ) and inhibition efficiency as a functions of Co-Amoxiclav concentration were calculated from the curves are shown in Table 2. It is evident from the figure that cathodic Tafel slopes (βc) 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]
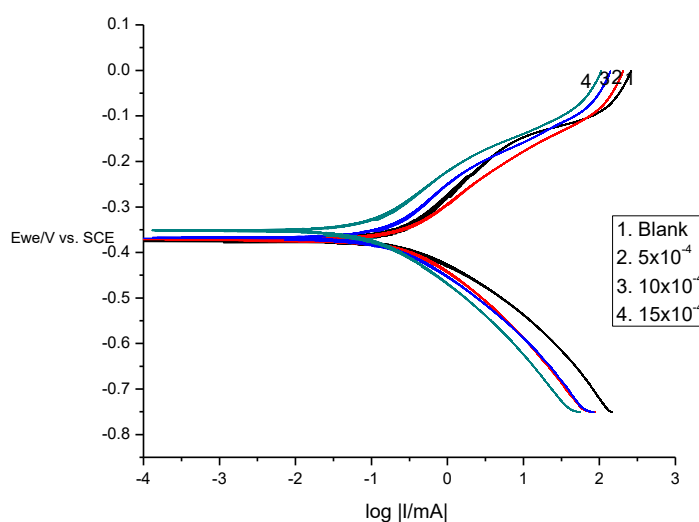
Figure 2. Potentiodynamic polarization curves for mild steel in 1 N HCl with different concentrations of Co-Amoxiclav.

It is observed that the inhibition efficiency increased with increasing Co-Amoxiclav 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 mV with respect to E, the inhibitor can be seen as a cathodic or anodic type, (ii) if displacement in E is < 85 mV, the inhibitor can be seen as mixed type. In our study the maximum displacement was 16 mV, which indicates that Co-Amoxiclav 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 15×10^{-4} M solution of Co-Amoxiclav.

Table 2. Electrochemical parameters and inhibition efficiency for corrosion of mild steel in 1 N HCl obtained by polarization method.

| Conc. (M)	E_{corr} (mV *vs* SCE)	I_{corr} (μA cm^{-2})	βa (mV dec^{-1})	βc (mV dec^{-1})	Surface Coverage (θ)	I.E. (%)
Blank	−355	412	143	125	–	–
5×10^{-4}	−354	255.44	109	147	0.3252	38.0
10×10^{-4}	−333	91.46	100	132	0.6577	77.8
15×10^{-4}	−321	49.44	89	136	0.8058	88.0

3.3. Electrochemical Impedance Spectroscopy (EIS) studies

Corrosion inhibition of mild steel in 1 N 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 1 N HCl with and without addition of different concentrations of Co-Amoxiclav are shown in the Figure 3. It is observed from the Figure that at all concentration range of Co-Amoxiclav 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 (Figure 3a), 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 semicircle 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].

Table 3. Electrochemical parameters and inhibition efficiency for corrosion of mild steel in 1 N HCl obtained by impedance method.

Concentration (M)	R_{ct} (Ω cm²)	C_{dl} (F cm^{-2})	Surface coverage (θ)	Inhibition efficiency (%)
Blank	79	0.410	–	–
5×10^{-4}	112.7	0.284	0.308	38.0
10×10^{-4}	230.2	0.090	0.78	78.0
15×10^{-4}	400.6	0.05	0.878	87.8
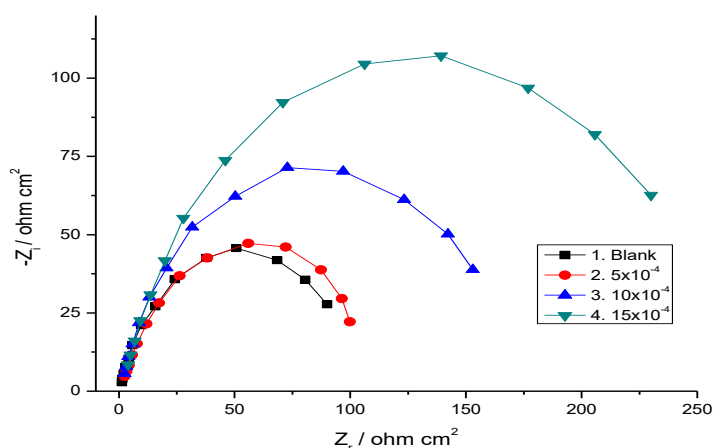
Figure 3: Nyquist plot of mild steel in 1 N HCl with different concentrations of Co-Amoxiclav.
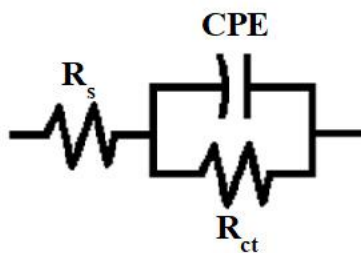
Figure 3a. Electrical equivalent circuit.

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 Co-Amoxiclav molecules

function by adsorption on metal surface and thereby causing the decrease in C_{dl} values and increase in R_{ct} values.

3.4. 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 (ϕc) [41] by the equation

$$\phi c = E_{corr} - E_{q=0}$$

Where $E_{q=0}$ is the potential of zero charge (pzc). The value of E_{corr} obtained in HCl is −355 mV *versus* SCE. In HCl solution Co-Amoxiclav acts as a protonated species. This protonated species are adsorbed directly on the metal surface through chloride atoms 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 ϕc is +175 mV *versus* SCE, so the metal surface acquires high positive charge as indicated below:

$$\phi c = E_{corr} - E_q = -355 \text{ mV} - (530 \text{ mV}) = +175 \text{ mV}.$$

Since the surface becomes positive charge due to the ϕc value is equal to + 175 mV, the adsorption of cationic Co-amoxiclav species does not occur and the adsorption of chloride ions take place and surface attains negatively charged. Now due to the electrostatic attraction, the protonated Co-Amoxiclav atoms are physically adsorbed on the mild steel surface and thereby offering high inhibition by Co-Amoxiclav molecules. Co-Amoxiclav molecules also adsorbed via their planar *p*-orbitals on the metal surface containing unfilled d-orbitals to inhibit the corrosion of steel surface.
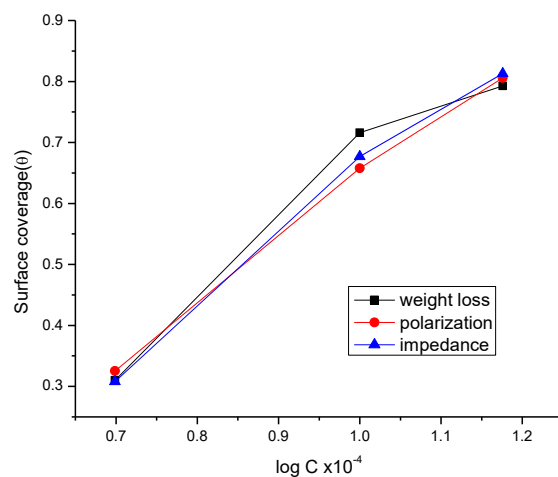
3.5. Adsorption isotherm

The degree of surface coverage (θ) for different concentrations of inhibitor in 1 N 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.

3.6.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).

Figure 4. Temkin adsorption isotherm for different concentrations of Co-Amoxiclav in 1 N HCl.

The corrosion inhibition of mild steel in 1 N 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 Figure 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 1 N 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 Co-Amoxiclav the reflectance percentage decreased only to small extend. This confirms that the surface characteristics are not altered more due to the formation of film on the surface [43]. The reflectance percentage increased as the concentration of inhibitor increased due to the increase in thickness of the film formed.

3.7. 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].
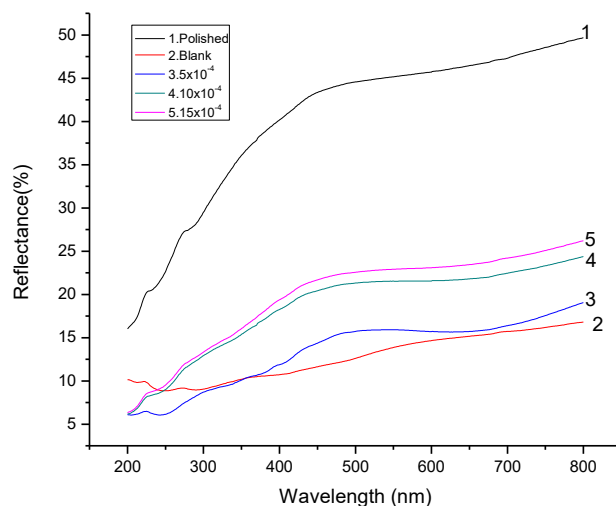
Figure 5. UV Reflectance curves for Mild Steel in 1 N HCl solution with different concentrations of Co-Amoxiclav.

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

Concentration of inhibitor	%IE	Permeation current μA
Blank	–	18.5
5×10^{-4}	38.00	11.12
10×10^{-4}	78.00	3.89
15×10^{-4}	87.88	1.25

4. Conclusion

i)   Co-Amoxiclav acts as a good inhibitor for the corrosion of mild steel in 1 N HCl.

ii) Potentiodynamic curves reveals that Co-Amoxiclav is a mixed type of inhibitor.

iii) The results obtained form weight loss, impedance and polarization studies are in good agreement with each other.

iv) The adsorption of Co-Amoxiclav 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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