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Electrochemical Investigation of The Effect of Penicillin G Benzathine as a Green Corrosion Inhibitor For Mild Steel

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ABSTRACT

In this paper, the effect of penicillin G benzathine (PGB) drug as a green corrosion inhibitor on mild steel in 1.0 M hydrochloric acid solution has been investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The inhibition efficiency (IE) was found to increase with increasing inhibitor concentration. Potentiodynamic polarization measurements indicated that PGB is a mixed type inhibitor. The results of potentiodynamic polarization and EIS measurements demonstrated that the adsorption of PGB on mild steel in 1.0 M HCl follows Langmuir isotherm. The calculated values of free energy indicated that both physical and chemical adsorption take place. The IE values obtained from EIS measurements show a reasonable agreement with those obtained from potentiodynamic polarization method. *Prog. Color Colorants Coat. 12 (2019), 15-23© Institute for Color Science and Technology.*

1. Introduction

Corrosion inhibitors are substances that, when added in small concentrations to corrosive media, decrease or prevent the reaction of metal with the media. Although many organic inhibitors demonstrate the high inhibition efficiencies, they are mostly toxic and harmful to the environment [1]. Saleh reported that hexadecyl pyridinium bromide (HDPB) as a cationic surfactant shows high inhibition efficiency for the corrosion of low carbon steel [2]. However, cationic surfactants are known of their toxicity and carcinogenicity in addition to their high cost. Recently, researchers have paid attention to the development of non-toxic and green corrosion inhibitors, such as plant extracts and drugs to obviate the harmful effect of chemicals on environment [3]. Because of their non-toxic characteristics and negligible negative impacts on the aquatic environment, drugs seem to be the ideal candidates to replace traditional toxic corrosion inhibitors [4-11].

Liang et al. have investigated the inhibition performances of four penicillin derivatives, including penicillin G, oxacillin, penicillin V and amoxicillin as organic corrosion inhibitors for mild steel in 1.0 M HCl solution by weight loss measurement and Tafel polarization technique [7]. The electrochemical results revealed that the inhibition efficiency follow the order: oxacillin>amoxicillin>penicillin V>penicillin G.

Golestani et al. investigated the effect of penicillin G, ampicillin and amoxicillin drugs on the corrosion behavior of carbon steel in 1.0 M HCl solution using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical noise techniques [8]. There was a case of mixed mode of adsorption here but while penicillin was adsorbed mainly through chemisorption, two other drugs were adsorbed mainly

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through physisorption.

Soltaninejad et al. found that penicillin G showed the best inhibition effect on mild steel at 10 mM concentration in 3.0 M H_3PO_4 solution using potentiodynamic polarization and EIS techniques [9].

Inhibition effects of irbesartan drug on mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 solutions have been investigated by open circuit potential (OCP) curves, Tafel and linear polarization curves, and electrochemical impedance spectroscopy [11]. Maximum corrosion inhibitions of 94% and 83% have been achieved at 300 ppm irbesartan concentration in HCl 1 M and H_2SO_4 0.5 M, respectively.

Singh et al. have investigated the use of expired atorvastatin for corrosion inhibition of mild steel in HCl 1 M solution using weight loss, EIS, and potentiodynamic polarization methods [12].

Kumar et al. have shown that the traces of a semi-synthetic antibiotic, called cloxacillin, inhibited the corrosion of mild steel in acid medium [13]. They have evaluated the inhibitory action of cloxacillin using weight loss, Tafel polarization, electrochemical impedance spectroscopy, and hydrogen permeation studies.

Raja and his co workers proved that the dissolution behavior of SS304 pipes in 2M sulfuric acid with green inhibitor, namely neomycin, as corrosion inhibitor using mass loss, potentiodynamic polarization and electrochemical impedance spectroscopy studies [14].

The present paper studies the inhibition action of penicillin G benzathine (PGB) (Scheme 1) on corrosion of mild steel in HCl 1 M solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The choice of this inhibitor as corrosion inhibitor is based mainly on its nontoxic properties and high solubility in acidic media.

2. Materials and Methods

2.1. Materials

Penicillin G benzathine was obtained from Sigma Aldrich Co. and used without any further purification. Figure 1 shows the chemical structure of this antibacterial drug. The employed working electrodes (WEs) were prepared from mild steel with the chemical composition (wt.%) of: C (0.15), Mn (0.73), Si(0.72) and Fe (98.4).

2.2. Methods

Potentiodynamic polarization and EIS measurements have been used to study the corrosion behavior of mild steel in 1 M HCl solution without and with doping by PGB at different concentrations. The aggressive solutions, 1 M HCl, were prepared by dilution of 37% HCl in distilled water. The stock solution of PGB (10 mM) was diluted to a certain concentration of PGB. The inhibitor concentration in the acid solution was in the range of 0.05 mM to 1 mM. Before performing experiments, the specimens were connected to a copper wire at one end sealed using resin, with the other end that it exposed as the WEs surface. The working surface was polished by wet abrasive papers through 600-2500 grade, washed with distilled water, degreased with ethanol, and finally dried in air.

Potentiodynamic polarization and EIS experiments were conducted using Autolab 302N potentiostat with Nova 1.6 software. The measurements were conducted in a conventional three-electrode cell. A platinum rod was used as the counter electrode and a saturated (KCl) Ag/AgCl electrode as reference electrode. To obtain the stabilized open circuit potential (OCP), the samples were immersed in the solution for 30 min before potentiodynamic polarization and EIS measurements.

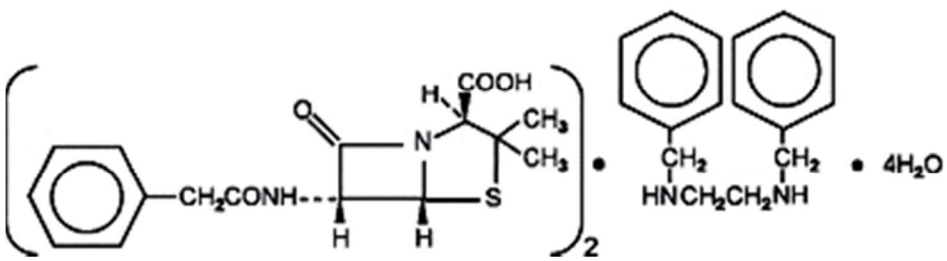

Figure 1: The molecular structure of penicillin G benzathine.

Polarization curves were recorded at a scan rate of 1 mV/s, and 1.9 Nova software was used for determination of corrosion current densities and polarization parameters. A sinusoidal potential perturbation of 10 mV versus OCP was used in the EIS measurements and a frequency range from 10 mHz to 100 kHz was employed. Nyquist plots from the impedance data were also analyzed using 1.9 Nova software.

3. Results and Discussion

3.1. Potentiodynamic polarization

Figure 2 shows the potentiodynamic polarization curves of mild steel in 1 M HCl solution in the absence and presence of various concentrations of inhibitor. The relevant parameter values are listed in Table 1 as corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a, β_c). It is clear that corrosion current density decreases as the concentration of inhibitor increases. The change in the values of β_c in the presence of inhibitor clearly indicates the effect of PGB on the kinetics of hydrogen evolution. The shift in the anodic Tafel slope (β_a) values may be due to the adsorption of inhibitor molecules onto the mild steel surface [15]. Therefore, addition of inhibitor to acid media affects both cathodic and anodic branches of the potentiodynamic polarization curves. So, it behaves as a mixed inhibitor.

Table 1: Polarization parameters and the corresponding inhibition efficiencies for mild steel in 1.0 M HCl containing different concentrations of penicillin G benzathine.

C /mM	i_{corr}/µA.cm^{-2}	-E_{corr}/mV	β_a/mV.dacade^{-1}	β_c/mV.dacade^{-1}	IE_P(%)
0	2370	442	142	226	-
0.05	505	452	103	158	79
0.1	371	439	96	157	84
0.5	120	442	93	131	95
1.0	90	443	94	122	96

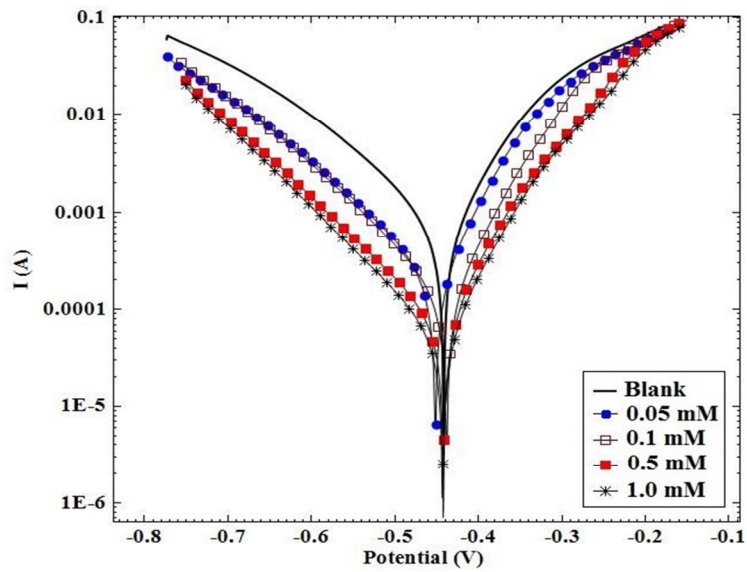

Figure 2: Tafel polarization curves of mild steel in 1 M HCl solution containing different concentrations of Penicillin G benzathine.

Generally, if the displacement in the absolute value of E_{corr} is more than 85 mV with respect to E_{corr} of the blank, the inhibitor can be regarded as cathodic or anodic type and if the displacement in E_{corr} is less than 85 mV, the inhibitor can be considered as a mixed type [7, 16]. In the present study, the shift in E_{corr} values is about 10 mV for the inhibitor, indicating that PGB has acted as a mixed inhibitor which is further evidenced from shifting of both cathodic and anodic Tafel slopes.

Table 1 also presents the values of the corrosion inhibition efficiency (IE) obtained from the following equation:

$$IE_P(\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \qquad (1)$$

where i_{corr} and i'_{corr} are corrosion current densities in the uninhibited and inhibited cases, respectively. The IE_P values show that the inhibition is more pronounced with increasing inhibitor concentration. These results also show that this drug acts as an effective corrosion inhibitor.

To calculate the surface coverage, θ, it was assumed that the inhibition efficiency is due mainly to the blocking effect of the adsorbed species, hence θ=IE(%)/100 [17]. Here, an attempt was made to test the Langmuir, Temkin and Frumkin isotherms having the following relationships:

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad \text{(Langmuir)} \qquad (2)$$

$$\ln C = -\ln K + a\theta \qquad \text{(Temkin)} \qquad (3)$$

$$\ln \frac{\theta}{C(1-\theta)} = \ln K + a\theta \qquad \text{(Frumkin)} \qquad (4)$$

where θ is the surface coverage, C is the inhibitor concentration, K is the adsorption equilibrium constant and a is the molecular interaction constant expressing the interaction between adsorbed and adsorbing molecules. The Langmuir adsorption isotherm was found to fit well with the experimental data (Figure 3).

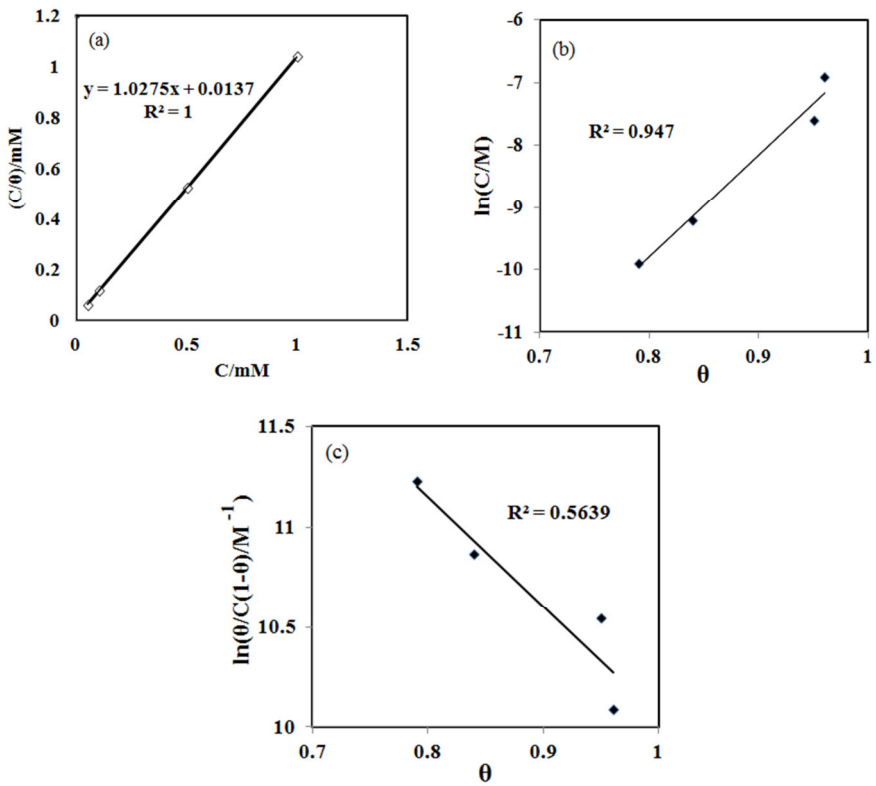

Figure 3: Adsorption isotherms for mild steel in 1 M HCl solution at the presence of different concentrations of penicillin G benzathine from polarization data (a) Langmuir (b) Temkin (c) Frumkin.

Straight line was obtained after plotting C/θ versus C (Figure 3a). The correlation coefficient is close to 1.0, confirming that the adsorption of PGB obeys the Langmuir isotherm. This isotherm is based on the assumption that all the adsorption sites are equivalent and the particle binding occurs independently from the nearby sites being occupied or unoccupied.

3.2. Electrochemical impedance spectroscopy

Nyquist plots of EIS for mild steel in 1 M HCl in the absence and presence of various concentrations of PGB are shown in Figure 4. In these spectra, variation of impedance response from mild steel after addition of inhibitor to the acid media is remarkable. Increasing the concentration of antibacterial drug shifted the charge transfer resistance to higher values. Table 2 lists impedance parameters in the absence and presence of different concentrations of penicillin G benzathine.

Figure 5 shows the electrical equivalent circuit employed to analyze the impedance plots. In Figure 5, R_s is the solution resistance and R_{ct} is the charge transfer resistance. The impedance of the constant phase element (CPE) is defined as follows [18]:

$$Z_{CPE} = \frac{1}{Y_0(jw)^n} \quad (5)$$

where Y_0 is a proportional factor, j equals $\sqrt{-1}$, w is the angular frequency and n is the phase shift. For $n = 0$, Z_{CPE} represents a resistance with $R = Y_0^{-1}$, for $n = 1$ a capacitance with $C = Y_0$, for $n = 0.5$ a Warburg element and for $n = -1$ an inductive with $L = Y_0^{-1}$ [19].

Table 2: Impedance parameters and the corresponding inhibition efficiency values for mild steel in 1 M HCl containing different concentrations of penicillin G benzathine.

C /mM	R_s/Ω.cm^2	R_{ct}/Ω.cm^2	n	C_{dl}/μF.cm^{-2}	IE_{EIS}(%)
0	1.4	18.5	0.852	152	-
0.05	1.6	48	0.888	85	62
0.1	1.5	85	0.885	55	78
0.5	1.3	205	0.885	35	91
1.0	1.4	287	0.884	30	94

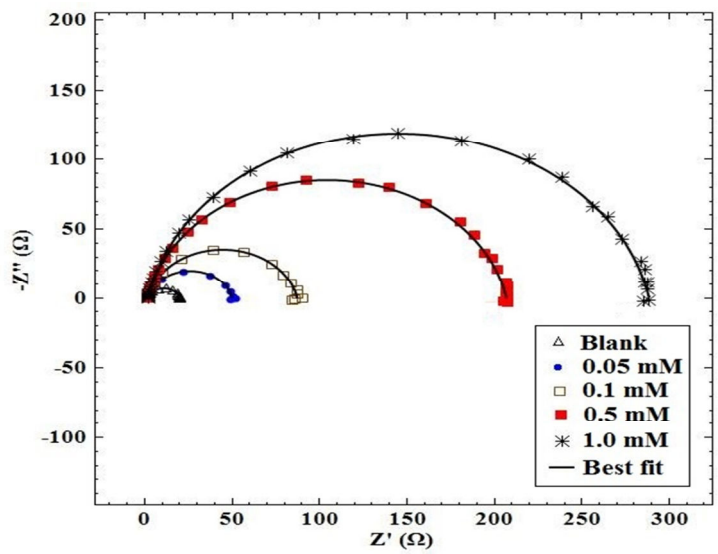

Figure 4: Nyquist plots for mild steel in 1 M HCl solution in the presence of different concentrations of penicillin G benzathine.

Because it was observed that n was closely near 1 (Table 2), the CPE obeys the capacitive behavior. Inspection of Figure 4 reveals that the addition of inhibitor increases the capacitive loop diameter of the Nyquist plots without affecting their characteristic features [15]. This means that the inhibition action of the inhibitor is due to its adsorption on the steel surface without altering the corrosion mechanism.

The data of Table 2 shows that the magnitude of R_{ct} increased while that of C_{dl} decreased with increasing the inhibitor concentration. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of inhibitor molecules on the steel surface decreases its electrical capacity as they displace the water molecules and other ions originally adsorbed on the surface. The decrease in this capacity with increasing the inhibitor concentration may be attributed to the formation of a protective adsorption layer on the electrode surface [15]. The thickness of this protective layer (d_{org}) is related to C_{dl} in accordance with Helmholtz model, given by the following equation [20]:

$$d_{org} = \varepsilon_0 \varepsilon_r A / C_{dl} \quad (6)$$

where ε_0 is the vacuum dielectric constant, ε_r is the relative dielectric constant and A is the effective surface area of the electrode. Decrease in the C_{dl}, which can be resulted from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggested that the inhibitor molecules act as the adsorption at the metal/solution interface. Thus, the change in C_{dl} values was caused by the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, decreasing the extent of the metal dissolution.

Inhibition efficiencies in Table 2 were calculated through the following expression:

$$IE_{EIS}(\%) = \frac{R_{ct}^{'} - R_{ct}}{R_{ct}^{'}} \times 100 \quad (7)$$

where R_{ct} and $R_{ct}^{'}$ represent the charge transfer resistance before and after addition of the inhibitor to the corrosion media, respectively. Inhibition efficiency increased with inhibitor concentration. This may be due to the increase in the surface coverage on the mild steel by the inhibitor, which led to the increase in inhibition efficiency [16]. By comparing the results with those of Table 1, one can conclude that a satisfactory agreement is found with the inhibition efficiencies obtained via potentiodynamic polarization measurements. The plots for each isotherm show that the EIS data agree with the Langmuir isotherm (Figure 6).

3.3. Thermodynamic parameters

The value of adsorption equilibrium constant, K_{ads}, is calculated from the reciprocal of the intercept of Langmuir adsorption isotherm line. The free energy of the adsorption of inhibitor on mild steel surface can be evaluated using the following equation [8]:

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \quad (8)$$

where 55.5 is the molar concentration of water in the solution (mol.L^{-1}), R is the gas constant (8.314 J K^{1}. mol^{1}) and T is the absolute temperature (K). The values of K_{ads} and ΔG_{ads} are derived from Langmuir adsorption isotherms for the studied inhibitor (Figures 3 and 6). Table 3 summarizes K_{ads} and ΔG_{ads} values obtained through Tafel polarization and electrochemical impedance measurements. Satisfactory agreement is found for ΔG_{ads} values obtained by different methods. Due to logarithmic relationship between K_{ads} and ΔG_{ads} values, some differences are observed in K_{ads} values obtained from different methods.

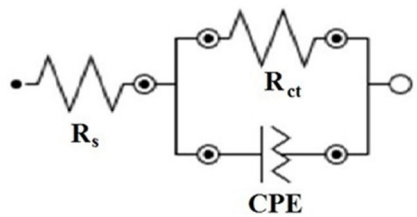

Figure 5: The equivalent electrical circuit of the impedance data.

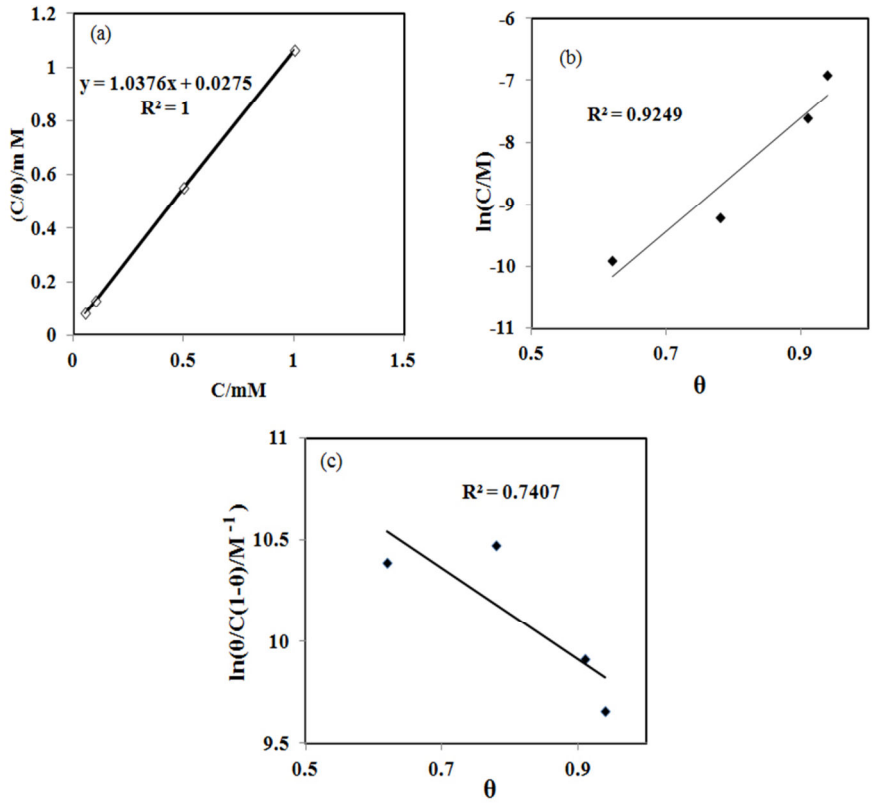

Figure 6: Adsorption isotherms for mild steel in 1 M HCl solution at the presence of different concentrations of penicillin G benzathine from impedance data (a) Langmuir (b) Temkin (c) Frumkin.

Generally, ΔG_{ads} around −20 kJ mol^{-1} or less negative values are consistent with the electrostatic interaction between charged molecules and the charged metal surface (physisorption); values around −40 kJ mol^{-1} or more negative involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of metal bond (chemisorption) [21]. In the present work, the calculated ΔG_{ads} values are the intermediate case indicating that the adsorption of inhibitor molecules is not merely physisorption or chemisorption, but obeying a comprehensive adsorption (both physical and chemical). Table 4 shows satisfactory agreement between IE% values acquired from two electrochemical methods.

The IE_p values for some different inhibitors reported in other published works on mild steel in 1 M HCl solution are gathered in Table 5 for comparison. Based on the data in Table 5, PGB can be used as an efficient inhibitor for mild steel in HCl solution.

Table 3: The values of K_{ads} and ΔG_{ads} corresponding to polarization and EIS data in 1 M HCl solution.

Tafel		EIS	
K_{ads} (M^{-1})	ΔG_{ads} (kJ.mol^{-1})	K_{ads} (M^{-1})	ΔG_{ads} (kJ.mol^{-1})
72993	-37.7	36363	-36.0

Table 4: The values of IE% corresponding to polarization and EIS data in 1 M HCl solution.

C/mM	IE_p%	IE_{EIS}%
0.05	79	62
0.1	84	78
0.5	95	91
1.0	96	94

Table 5: The values of IE_p% of different inhibitors corresponding to mild steel in 1 M HCl solution.

Inhibitor	0.05 mM	0.1 mM	0.5mM	1.0mM	Ref.
Penicillin	-	64.0	74.2	88.1	[8]
Oxacillin	82.1	93.1	-	93.2	[7]
Ampicillin	-	46.9	62.4	84.5	[8]
Irbesartan	-	71	92	-	[11]
PGB	79	84	95	96	This work

4. Conclusions

The adsorption and inhibition effect of antibacterial drug PGB on the corrosion behavior of mild steel in 1 M HCl was studied using electrochemical techniques. The antibacterial drug offers interesting possibilities for corrosion inhibition because of its nontoxic properties and high solubility in acidic media. Results obtained from potentiodynamic polarization and EIS measurements demonstrated that the adsorption of PGB on mild steel in 1 M HCl follows Langmuir isotherm. The calculated values of free energy indicated that both physical and chemical adsorption take place. The IE and ΔG_{ads} values obtained from EIS data for PGB show a reasonable agreement with those obtained from potentiodynamic polarization measurements.

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