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Electrochemical Investigation of the Inhibitory Action of Ciprofloxacin Drug on the Acid Corrosion of Mild Steel

I. A. Akpan* N. O. Offiong
Corrosion and Materials Science Laboratory, Department of Chemistry, University of Uyo
P. M. B. 1017, Uyo, Akwa Ibom State, Nigeria
*E-mail address of corresponding author: iaakpanchem2007@yahoo.com

Abstract
Electrochemical investigation of mild steel corrosion in acidic medium inhibited by an environmentally safe and commercially available low cost drug, ciprofloxacin, was carried out at room temperature. The results obtained show that the drug provided a good protection for mild steel in the acid medium investigated. The inhibition efficiency was found to increase with a corresponding increase in the concentration of the drug. The adsorption process that facilitated the inhibition mechanism was found to follow the Langmuir's adsorption isotherm.
Keywords: linear polarization resistance (LPR), corrosion inhibition, mild steel, ciprofloxacin drug

1. Introduction

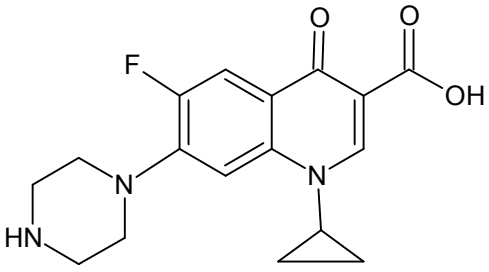
The study of corrosion processes and their inhibition is a very active area of research [1]. Recently, serious concerns and awareness have been created in the literatures over the high cost, toxicity and hazardousness of some corrosion inhibitors [2-6]. For these reasons, attention of researchers has been shifted to the use of non-hazardous, cost-effective and easily accessible corrosion inhibitors, especially drugs [7, 8]. This trend of interest may have been triggered due to the fact that inhibitors extracted from plants had to go through rigorous processes of isolation, purification, characterization and further synthesis as well as institution of experimental tests to ascertain the applicability of such an inhibitor.
Since most drugs are known to posses chemical structures which contain potential adsorption sites for effective inhibition, they have been found as useful alternative as corrosion inhibitors.
As part of our contribution to the quest of fighting corrosion, the objective of the present work is to carry out electrochemical investigation of the inhibitory action of ciprofloxacin drug on the corrosion of mild steel in hydrochloric acid medium.

2. Experimental

The experimental model developed for this study was implemented using the electrochemical linear polarization method. It has been said that electrochemical methods are sensitive and widely used for corrosion monitoring [9].

2.1 Inhibitor

The inhibitor used in this study was an antibiotic drug with common name: ciprofloxacin while its systematic name is 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-quinoline-3-carboxylic acid. The molecular formula of the drug is $C_{17}H_{18}FN_3O_3$ with molecular mass of 331.346g/mol. Ciprofloxacin has the chemical structure shown below:



Ciprofloxacin

The tablets of ciprofloxacin were obtained from a local pharmacy and were used without further purification or modification. From the mass of the drug samples and it molecular weight relation, appropriate concentrations of the drug were prepared by dilution.

2.2 Corrosive solution

The corrosive medium used in this study was 0.1M HCl. It was prepared by appropriate dilution for analytical grade HCl reagent with double distilled water without further purification.

2.3 The specimen

Mild steel (98% Fe) used for this investigation was obtained and identified locally. The metal sheets were mechanically press cut into rectangular coupons of about 3cm by 3cm. The thickness of the metal was 0.1cm. In the electrochemical measurements, the working electrode was cut from the mild steel. The coupons were used without further polishing. However, they were degreased in acetone, washed with double distilled water and finally dried.

2.4 Electrochemical measurements

A conventional three-electrode system consisting of mild steel as working electrode, carbon as an auxiliary electrode, carbon as an auxiliary electrode and saturated calomel electrode (SCE) as reference electrode was used for the measurements.

3. Results and Discussions

3.1 Linear polarization resistance

The electrochemical method employed in the study of the corrosion activity of mild steel in 0.1M HCl inhibited by ciprofloxacin drug was monitored via the linear polarization resistance (LPR) technique. Polarization measurements have become a useful and important research tool in investigation of variety of electrochemical phenomena [10]. In this method, the values for potential were plotted against that of current and calculations were obtained from the slopes of the initial linear region of the polarization curves [11]. After measuring the currents and potentials, a plot of the parameters are shown in figure 1.

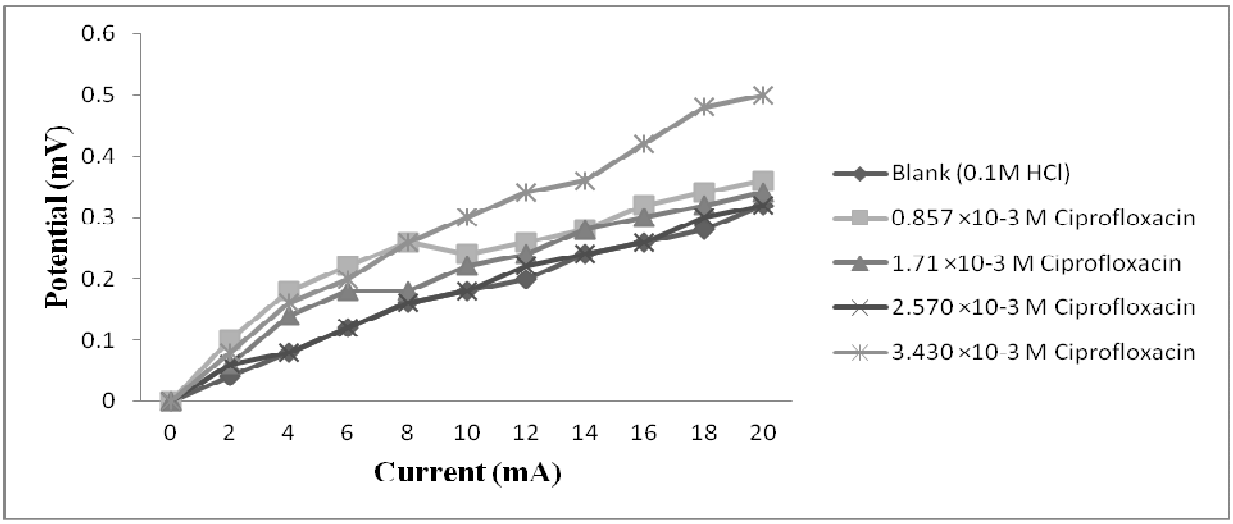


Figure 1: It shows the variation of applied potential and current change for mild steel corrosion in 0.1M HCl in the presence and absence of different concentrations of the inhibitor.

With the help of equation 1, the polarization resistance (Rp) were computed from the slopes of the initial regions of the polarization curves [12].

$$Rp = A \times (slope\ of\ plot\ of\ E\ versus\ I) \quad (1)$$

where A is the surface area of the electrode, E is the potential and I is the current.

The corrosion current densities (Icorr) were calculated from equation 2 [9, 13]. This was done to help give an insight about the extent of corrosion.

$$I_{corr} = \frac{B}{R_p} \quad (2)$$

where B is a proportionality constant, which equals 0.026V for a particular system [13].

The computation of Icorr gave access to the estimation of the percentage corrosion inhibition efficiency (%IE) via equation 3 [12].

$$\%IE = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} \times 100 \quad (3)$$

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

Observation of table 1 reveals that the corrosion current densities (Icorr) were higher in the free acid medium – meaning that corrosion rate was higher there. Again, it can be seen that the polarization resistance obtained for mild steel in the free acid solution as well as those containing different concentrations of the inhibitor indicate

that the drug significantly increased the resistance of the metal against corrosion.

Table 1: It shows corrosion parameters obtained from polarization measurements for mild steel in 0.1M HCl in the presence and absence of different concentrations of the inhibitor at 30°C.

System/Concentration	Rp (Ωcm^2)	Icorr (mA/cm^2)	Degree of surface coverage (Θ)	%IE
Blank (0.1M HCl)	0.013	201.55	-	-
0.857×10^{-3}M Ciprofloxacin	0.365	71.077	0.647	65
1.71×10^{-3}M Ciprofloxacin	0.576	45.14	0.776	78
2.57×10^{-3}M Ciprofloxacin	0.864	30.09	0.851	85
3.43×10^{-3}M Ciprofloxacin	1.152	22.57	0.888	89

Polarization resistance increases as the inhibition as the inhibition approaches maximum when the metal specimen apparently stops corroding [11]. The experimental data obtained for the polarization resistance (Rp) and corrosion current densities (Icorr) are consistent with the known theoretical basis for the method employed; that, corrosion current density (Icorr) has an inverse relationship with polarization resistance (Rp).

The values of the percentage corrosion inhibition efficiency shown in table 1 indicate that the polarization resistance (Rp), and in consequence, the ability of the metal to resist corrosion increased as the concentration of the inhibitor increased.

3.2 Adsorption isotherms

The available data have revealed that the action of corrosion inhibitors is due to adsorption of the inhibitor molecules on the surface of the corroding metal. The adsorption may be attributed to the nature and charge of the metallic surface, the type of the corrosive medium and the molecular structure of the inhibitor [14, 15].

The adsorption modes are usually confirmed from the fit of experimental data into the various adsorption isotherms. The calculated values of thr degree of surface coverage (Θ) which gave access to the estimation of the adsorption mode are given in table 1 and were determined using equation 4 [12].

$$\theta = 1 - \frac{(I_{corr})inhibited}{(I^{o}_{corr})unhibited} \qquad 4$$

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

As seen from table 1, the degree of surface coverage increased with increase in the inhibitor concentration. It may be assumed that the more molecules of the inhibitor were needed to effectively obtain a wider coverage area of the metallic surface.

In this study, it was found that the experimental data fits the Langmuir's adsorption isotherm shown in figure 2; where plots of log (Θ/(1-Θ)) versus the logarithm of the concentrations of the inhibitor produced a linear graph.

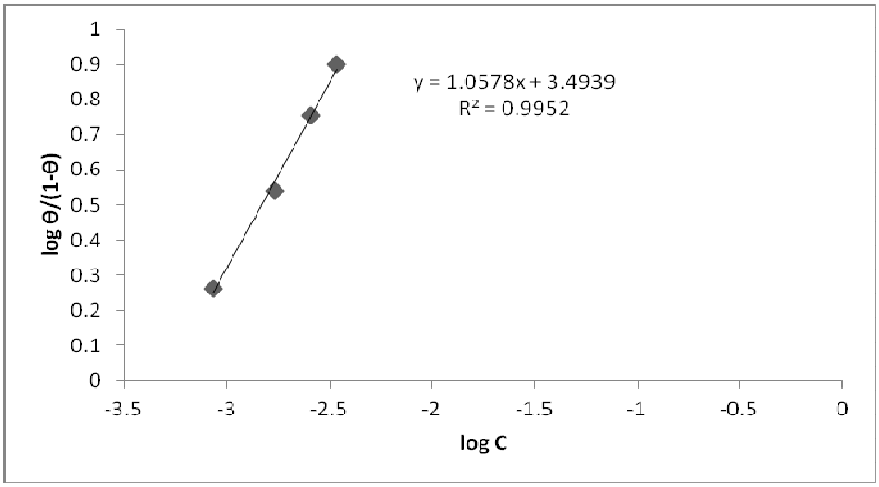


Figure 2: It shows Langmuir's adsorption isotherm for mild steel in 0.1M HCl containing various concentrations of ciprofloxacin drug as inhibitor.

Based on the experimental data obtained, it is of assumption that mild steel corrosion in 0.1M HCl was inhibited by ciprofloxacin drug by adsorption unto appropriate sites of the electrode surface [16]. The

Langmuir's adsorption isotherm assumes that there is no strong interaction between the adsorbed molecules and the metal surface [17].

3.3 Mechanism of inhibition

The action of ciprofloxacin as an inhibitor may be due to its large molecular weight [18], or interaction between the lone pairs of electrons available on F, O and probably N. However, interaction of the metallic surface with the lone pairs of electrons on all then nitrogen atoms in the molecule may be difficult due to their entrapment within the molecular structure of the compounds. This reduces the chances of having a proper orientation towards the metallic surface so as to produce effective coordination between the inhibitor-metal interface.

Conclusion

From the results of the investigation the following may be concluded,

1. Ciprofloxacin drug significantly increased the resistance of mild steel against corrosion in 0.1M HCl solution and therefore can be employed an environmentally safe, cost effective and easily accessible corrosion inhibitor for the metal.
2. The inhibition efficiency increased with increase in the concentrations of the inhibitor.
3. The adsorption process of ciprofloxacin under the investigated conditions was found to obey the Langmuir's adsorption isotherm.
4. The inhibitory action of the test drug signifies the action of its molecular structure.

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