Test of No Plac Expired Drug as Metallic Corrosion Inhibitor for Carbon Steel

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Abstract

Chemical and electrochemical techniques were used to test the expired **No Plac** medication as a corrosion inhibitor for carbon steel in 1.0 M HCl. The results showed that **No Plac** may play an essential function as a corrosion inhibitor for carbon steel. Due to the adsorption of drug molecules on the carbon surface, the protection efficiency increases with increasing drug concentrations. It was also discovered that the adsorption followed the Frumkin isotherm. The polarization results revealed that the expired medication inhibits both cathodic and anodic processes, indicating that it is a mixed inhibitor. The expired medication enhances polarization resistance by adsorbing on the metal/electrolyte contact, according to EIS test. Finally, the calculated thermal parameters showed the spontaneous and physical adsorption of the drug molecules on the metal surface, as well as the excellent role of the drug at different temperatures.

Keywords: Expired drug, Corrosion inhibition, Carbon steel.

1. Introduction

Large doses of expired or unused drugs prompted the investigation of their inhibitory properties. Some of them are incinerated and others are discarded in the sewers, polluting the atmosphere and the environment [1, 2]. Also, the expired medicines retain their properties beyond their expiration dates [3]. The inhibitory activity of the active ingredients of drugs has been studied in detail for their molecular physics towards metals via aromatic rings containing lone electron pairs, multiple bonds, N, O, or S atoms. It has been shown to enable physical or chemical interactions [6-13].

The aim of our study is to test the expired **No Plac** as corrosion inhibitor of carbon steel in acidic solution. This is done through electrical and chemical measurements, with the determination of the type of drug adsorption on the surface of the metal and the extent of its effect at different temperatures.

2. Materials and Methods
2.1. Materials

The used material was carbon steel with the composition w/w Cu 0.20%, C 0.28%, Si 0.22%, P 0.9%, Mn 0.53%, Ni 0.09%, Cr 0.8%, Mo 0.1%, S 0.6 %, Fe < 98.4%. The used hydrochloric acid (37.00%) was obtained from AL-Nasr Chemical Company, and the solutions were prepared using double distilled water to make a 1.0 M HCl solution as the aggressive medium for the experimental setup. The used inhibitor is **No Plac** Mouth Rinse, produced by Sigma/CityPharma, has the composition: Chlorohexidine digluconate + sod. Mono flouro phosphate + sod. Citrate + sod. Borate + dimethicone. Because of its high content of heteroatoms [15] and its status as a medical waste [16], the medication is suited for use as a corrosion inhibitor. The drug was used here without any further purification or extraction.

2.2. Weight Loss Technique

The carbon steel specimens are installed with the same dimensions (2.0 cm^3). All samples were polished with 800, 1000, 1200 emery papers, thoroughly washed with redistilled water and acetone, and dried. The weight loss was measured for carbon steel (the specimens were washed with distilled water, dried and weighed between two filter papers) after immersing it for specific periods of time (30, 60, 90 and 120 minutes) in 50 cm^3 volume of 1.0 M HCl solution alone and also with different concentrations of **No Plac** (5, 10, 15 and 20 ppm). The experiment is repeated three times, as well as the measurement to take the average measurement.

2.3. Electrochemical Techniques
2.3.1. Potentiodynamic Polarization

The potentiodynamic polarization curves were gained by scanning the carbon steel electrode in the range of -1000 to +1000 mV at scan rate of 1.0 mV/sec. From the Tafel plots, the corrosion potential (E_{corr}), the corrosion current density (i_{corr}) and the Tafel constants (β_a & β_c) were calculated. in 50 cm^3 volume of 1.0 M HCl solution alone and also with different concentrations of **No Plac** (5, 10, 15 and 20 ppm).

2.3.2. Electrochemical Impedance Spectroscopy

The Nyquist diagrams were gained by applying AC signs of 10 mV peak-to-peak amplitude on the carbon steel surface from frequency of 10^5 Hz to 0.1 Hz. The polarization resistance R$_p$, is obtained from Nyquist plots diameter. This is done in 50 cm^3 volume of 1.0 M HCl solution alone and also with different concentrations of **No Plac** (5, 10, 15 and 20 ppm).

3. Results and Discussion
3.1. Weight Loss Measurements

Fig (1) below shows the effect of **No Plac** concentration on the corrosion of carbon steel in 1.0 M HCl, as well as the effect of time exposure on the drug effectiveness. It is clear from the figure the positive effect of drug concentration on its efficacy, as well as the positive effect of time, despite its less

effect compared to the effect of concentration. This is due to the crowding of the drug components on the surface of the metal, which leads to their struggle for adsorption on the surface, which led to some effect on the time factor. The inhibition efficiency (IE%) were calculated from equation (1):

$$IE \% = 1 - (r_d / r_f) \times 100 \qquad (1)$$

where r_f and r_d are corrosion rates in (g / cm^2 h) in the absence and in the presence of a drug, respectively. The values of the corrosion rate and inhibition efficiency are shown in table (1).

No Plac drug is rich in elements such as nitrogen and oxygen, that are rich in electron pairs, for which is the reason for the adsorption of drug molecules on the surface of the metal, causing a reduction in the rate of corrosion by forming an insulating layer of the drug that protects the metal surface from acid attack.

3.2. Potentiodynamic Polarization

In this study, we tested the effect of adding **No Plac** to 1.0 M HCl solution on the potentiodynamic polarization curves of the immersed carbon steel as shown in Fig (2). The inhibition efficiency was calculated by using the following equation [18]:

$$IE \% = 1 - (i_d / i_f) \times 100 \qquad (2)$$

where, i_d and i_f are the corrosion current densities in the presence and absence of the tested drug, respectively.

By studying the figure, it becomes clear to us a clear decrease in the current density with the addition of increasing concentrations of the drug. Also, Table (2) shows that the corrosion current density (i_{corr}) decreases with the increasing concentration of the drug added. The potentiodynamic polarization curves allow us to study the corrosion mechanism, which is clearly not changed by adding the drug, as the polarization curves, after adding the drug, are parallel to the corresponding blank curve. It is also clear to us that the effect of the drug on the rate of corrosion is a mixed effect, as both the anodic and cathodic current densities decrease, in addition to the almost non-displacement of the corrosion potential (E_{corr}) with the addition of the drug [19-21].
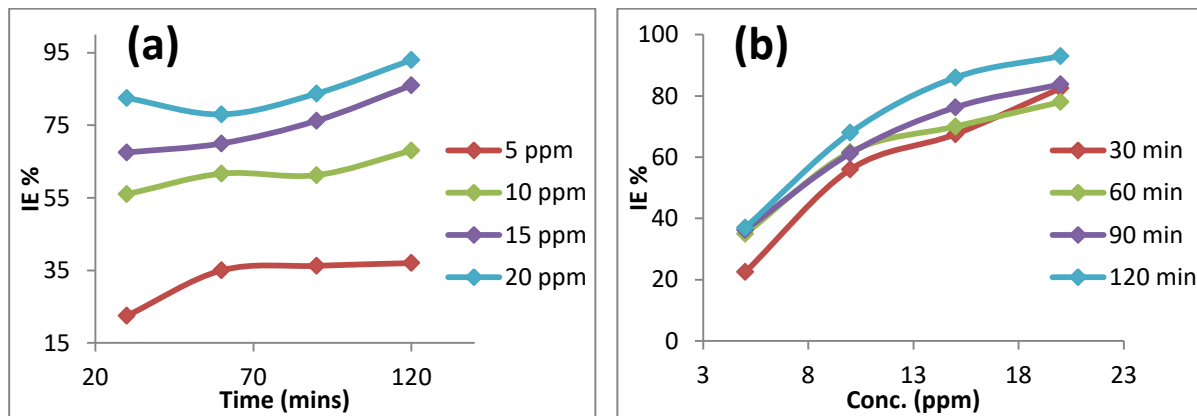

Fig (1) (a) Relation between exposure time and inhibition efficiency of different **No Plac** concentrations vs carbon steel corrosion in 1.0 M HCl. (b) Relation between **No Plac** concentration and its inhibition efficiency at different exposure times of carbon steel in 1.0 M HCl.

Table (1) the corrosion rate of carbon steel in 1.0 M HCl solution and the inhibition efficiencies of different concentrations of **No Plac** at different exposure times.

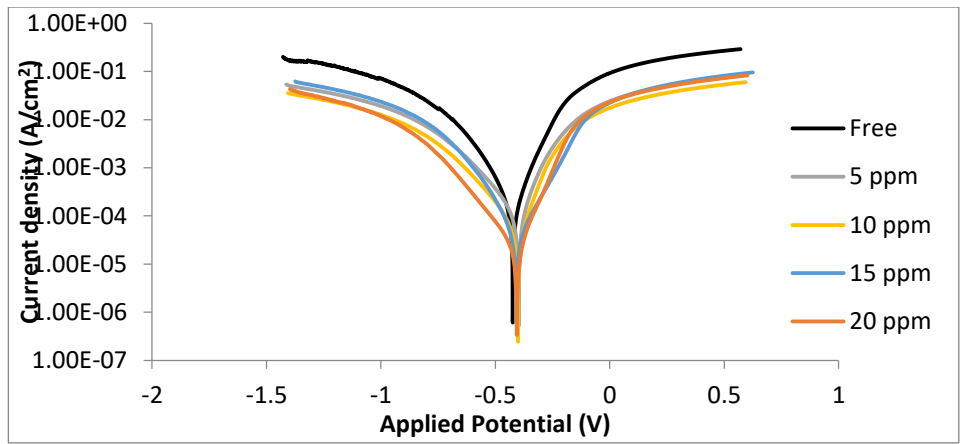| Solution	30 mins		60 mins		90 mins		120 mins	
	r (g/cm^2.h)	IE %	r (g/cm^2.h)	IE %	r (g/cm^2.h)	IE %	r (g/cm^2.h)	IE %
Free	0.02	-	0.03	-	0.04	-	0.05	-
5 ppm	0.0155	22.50	0.0195	35.00	0.0255	36.25	0.0315	37.00
10 ppm	0.0088	56.00	0.0115	61.67	0.0155	61.25	0.016	68.00
15 ppm	0.0065	67.50	0.009	70.00	0.0095	76.25	0.007	86.00
20 ppm	0.0035	82.50	0.0066	78.00	0.0065	83.75	0.0035	93.00

Fig. (2) Potentiodynamic polarization curves for carbon steel in 1.0 M HCl solution with different conc. of **No Plac** at 298 K and scan rate of 1.0 mV/sec.

Table (2) Electrochemical corrosion parameters of carbon in 1.0 M HCl solution and different concentrations of **No Plac** at 298 K and scan rate of 10 mV/sec.

Solution	ba (mV/dec)	-bc (mV/dec)	Ecorr, (mV)	icorr (μA)	Corrosion rate (mm/year)	IE %
Free 1 M HCl	117.17	161.38	-410.99	318.45	3.70	-
5 ppm No Plac	130.59	199.46	-426.59	160.06	1.86	49.74
10 ppm No Plac	127.82	148.10	-560.72	97.44	1.13	69.40
15 ppm No Plac	136.91	192.04	-420.99	70.87	0.82	77.75

3.3. Electrochemical Impedance Spectroscopy

Fig (3) shows the Nyquist plots obtained for carbon steel corrosion suppression in 1.0 M HCl solution containing different concentrations of No Plac at room temperature. An equivalent circuit (Randles circuit) was used for impedance analysis [22]. Table (3) shows various impedance parameters such as charge transfer resistance (R_P), solution resistance (R_s), and suppression efficiency (IE%).

The inhibition efficiency (IE%) of the drug was calculated from the following equation:

$$IE \% = 1- (R_{P (free)} / R_{P (drug)}) \times 100 \qquad (3)$$

The Nyquist plots give conclusive evidence of the excellent drug efficiency against carbon steel corrosion in 1.0 M HCl solution with the increase of this efficiency with drug concentration, as it is known that the value of the diameter of these plots is equivalent to the charge transfer resistance of the solution R_P. [23, 24]
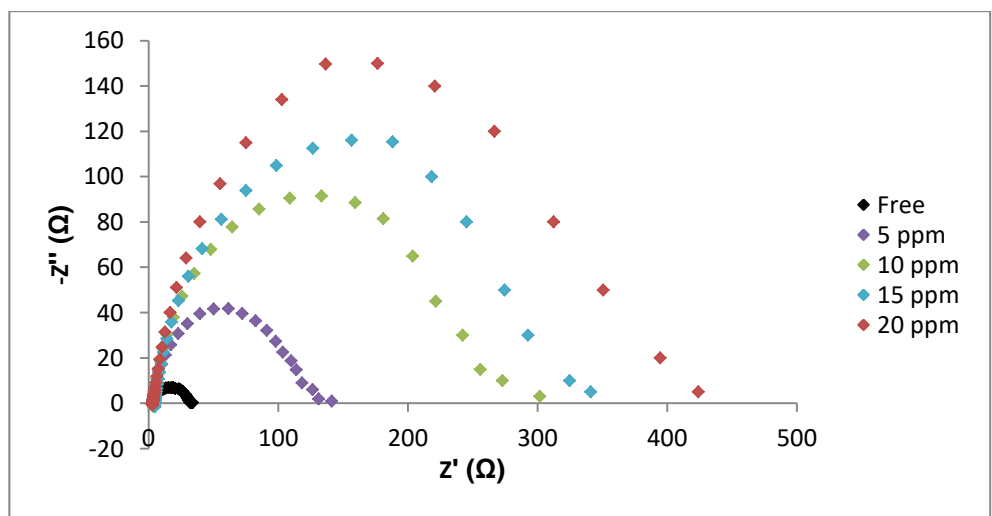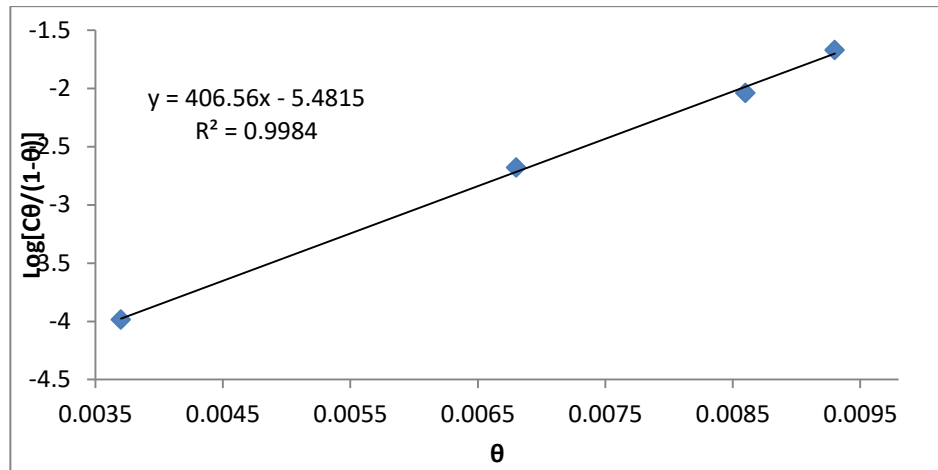

Fig. (3) Nyquist for carbon steel in 1.0 M HCl solution with different concentrations of **No Plac** drug at room temperature.

Table (3) EIS parameters for carbon steel in 1.0 M HCl solution with different concentrations **No Plac** drug at room temperature.

Solution	Rs (Ω)	Rp (Ω)	IE %
Free 1 M HCl	4.29	40.09	-
5 ppm No Plac	7.82	201.60	80.11
10 ppm No Plac	6.14	268.06	85.04
15 ppm No Plac	7.48	350.01	88.55
20 ppm No Plac	9.01	479.21	91.63

$$y = 406.56x - 5.4815$$
$$R^2 = 0.9984$$

Fig. (4) Langmuir Adsorption Isotherm for **No Plac** on carbon steel in 1.0 M HCl solution.

3.4. Adsorption Isotherm

The results of the study are more compatible with Frumkin adsorption isotherm [25]:

$$\log\left(\frac{\theta C_{drug}}{1-\theta}\right) = \log K + g\theta \qquad (4)$$

where θ is the surface coverage, K is the adsorption-desorption equilibrium constant, C_{drug} is the drug concentration and g is the adsorbate interaction parameter. Plotting $\text{Log}[C\theta/(1-\theta)]$ versus θ gave straight line, as shown in Fig (4). The straight line has an intercept of Log K, from which K was computed $(11.782 \times 10^{-3} \text{ ppm}^{-1})$. The standard free energy of adsorption $\Delta G°_{ads}$ is calculated according the following equation:

$$K = 1/C_{H_2O} \exp(-\Delta G°_{ads}/RT) \qquad (5)$$

where, R is the universal gas constant and C_{H_2O} is the density of water in mg L^{-1}. The calculated negative value of $\Delta G°_{ads}$ for **No Plac** (-23.231 kJ/mol) less than -40 kJ/mol indicates the spontaneous and physical adsorption process of drug molecules on the metal surface [19, 26, 27].

3.5. Thermodynamic Parameters

In this study, we tested the effect of **No Plac** drug adding on the Tafel polarization curves of carbon steel in 1.0 M HCl solution at different temperatures, Fig (5). We used Arrhenius and transition – state equations in the study:

$$CR = A \exp(-E_a/RT) \qquad (6)$$
$$CR = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \qquad (7)$$

where CR is the corrosion rate of copper in mm/y, Ea is the activation energy, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation.

From the potentiodynamic drawings below, we find that the corrosion of the metal increases with the increase in temperature, whether in the absence of the drug, and this is normal, as the increase in temperature helps to increase the rate of collision of the attacking acid atoms with the surface of the metal and thus the rate of corrosion increases, and also in the case of adding the drug to the acid solution. However, the corrosion rate at all tested temperatures is lower in the case of adding the drug, and that is obvious in the Arrhenius and transition-state curves. This is another evidence of the physical adsorption of drug molecules on the metal surface, as it can be explained by the hypothesis that increasing temperature causes the adsorption molecules to be released from the metal surface, and this is not possible with chemical adsorption [19].

By calculating the thermodynamic parameters, shown in table (4), we find a noticeable increase in the values of activation energy (Ea), the enthalpy of activation (ΔH^*) and the negative values of entropy (ΔS^*), which explains the decrease in the ease of metal corrosion due to increasing the energy barrier that precedes the corrosion process by the adsorption of drug molecules on the surface. The drug molecules create a random environment during the adsorption process, until they stabilize after making a protective layer for the metal [26, 28].
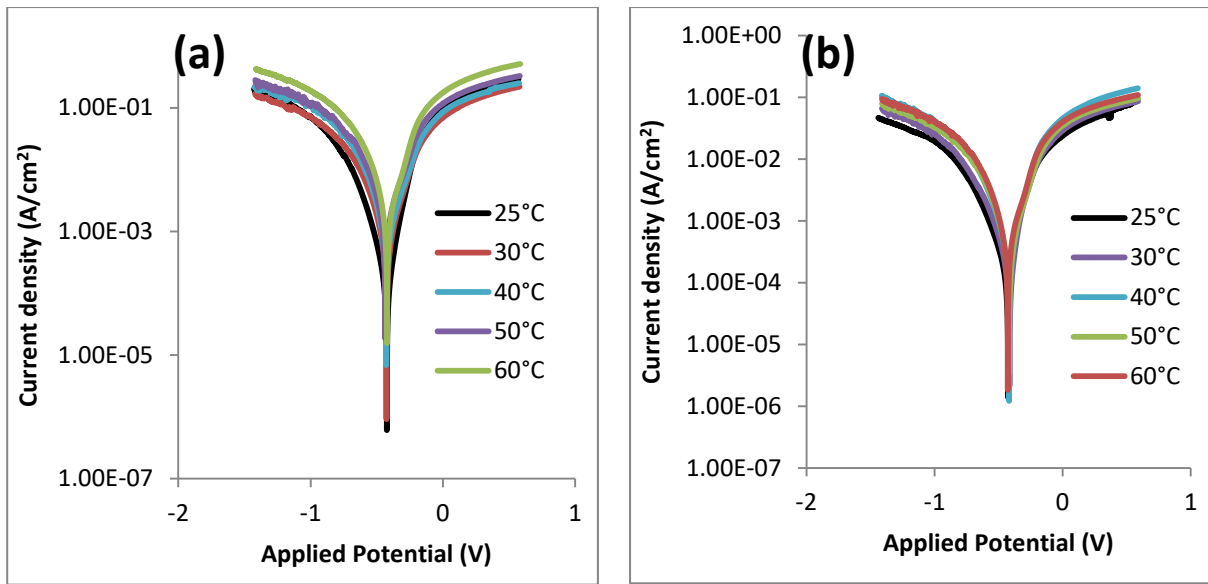
Fig. (5) Electrochemical polarization curves for carbon steel in (a) uninhibited 1.0 M HCl solution and (b) inhibited 1.0 M HCl solution with 20 ppm of **No Plac** at different temperatures and scan rate of 1.0 mV/sec.
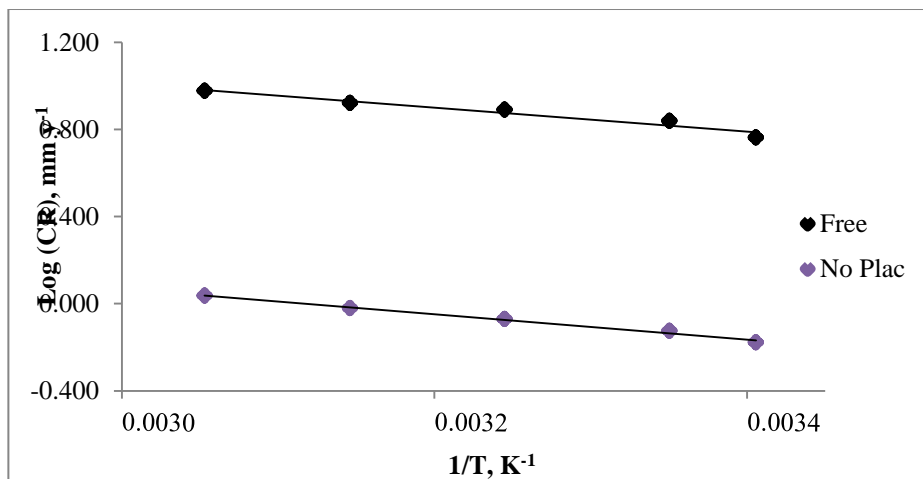

Fig. (6) Arrhenius plot for carbon steel in 1.0 M HCl solution without and with 20 ppm of **No Plac**.
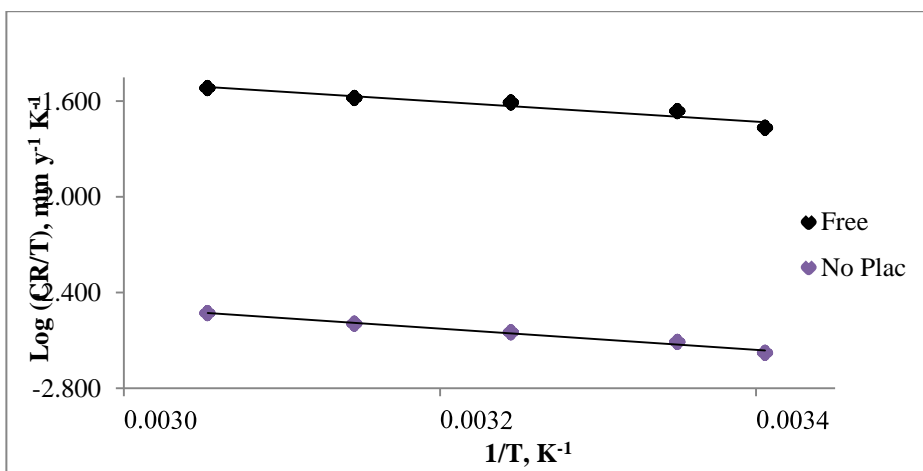

Fig. (7) Transition state plot for carbon steel in 1.0 M HCl solution without and with 20 ppm of **No Plac**.

Table (4) Activation parameters of the dissolution of carbon steel in 1.0 M HCl solution in absence and presence of 20 ppm of **No Plac** drug, individually, at different temperatures.

Solution	Ea*, kJ.mol^{-1}	ΔH*, kJ.mol^{-1}	-ΔS*, J.mol^{-1}.K^{-1}
Free 1 M HCl	10.577	7.961	203.177
20 ppm No Plac	11.166	8.549	219.563

4. Conclusion

- Expired **No Plac** was found to be a good corrosion inhibitor for carbon steel in 1.0 M HCl solution.
- The inhibition efficiency of **No Plac** against the carbon steel corrosion increases with concentration and decreases with rising temperature, indicating for the physical nature of its molecules' adsorption.
- The adsorption of **No Plac** constituents on carbon surface in 1.0 M HCl solution follows Frumkin isotherm.
- The adsorption process was physical and spontaneous due to the small negative value of $\Delta G°_{ads}$ calculated.
- **No Plac** acts as a mixed type of inhibitor, due to the polarization measurements.

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