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Adsorption and corrosion inhibition effect of benzodiazepine derivative on carbon steel in 2.0 M H_3PO_4 medium

T. Laabaissi[1], M. Bouassiria[1], H. Oudda[1*], H. Zarrok[1*],
A. Zarrouk[2], A. Elmidaoui[1], L. Lakhrissi[3], B. Lakhrissi[3], E.M. Essassi[4], R. Touir[5,6]
[1]*Laboratoire des procèdes de séparation, Faculté des Sciences, Université Ibn Tofail, Kenitra, BP 133, Kenitra, Morocco.*
[2]*LCAE-URAC 18, Faculté des Sciences, Université Mohammed Premier, Oujda, Morocco*
[3]*Laboratoire d'Agroressources et Génie des Procédés, Université Ibn Tofail, Faculté des Sciences, Département de Chimie, B.P. 133, Kénitra, Morocco*
[4]*Laboratoire de Chimie Organique Hétérocyclique, Université Mohammed V, Faculté des Sciences, B.P. 1014, Rabat, Morocco*
[5]*Laboratory of Materials, Electrochemistry and Environment, Faculty of Science, Ibn Tofail University, PB 133-14050, Kénitra, Morocco.*
[6]*Centre Régional des métiers de l'éducation et de la formation (CRMEF), Avenue Allal Al Fassi, Madinat Al Irfane BP 6210 Rabat, Morocco.*

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**Corresponding author. E-mail: hzarrok@gmail.com, ouddahassan@gmail.com*

Abstract

Corrosion inhibition performance of 4-(2-oxo-propylidene)-1,5-benzodiazepin-2-one (OPBz) on the corrosion behaviour of carbon steel in 2 M phosphoric acid solution was investigated by through potentiodynamic polarization technique and electrochemical impedance spectroscopy. The inhibition efficiency results of OPBz were observed to increase with increase in OPBz concentration, but decreases with increase in temperature. Polarization studies showed that the inhibiting compound is a mixed type inhibitor. The inhibition mechanism of the compound was discussed in view of its electrode blocking effect through adsorption of the inhibitor molecules. The compound obeyed the Langmuir adsorption isotherm. Thermodynamic parameters of activation were calculated and discussed. Data obtained for inhibition efficiency from the three test techniques are in reasonably good agreement.

Keywords: Carbon steel, H_3PO_4, Benzodiazepine derivative, Corrosion inhibition, EIS.

1. Introduction

Carbon steel is widely applied as construction material in many industries due to its exceptional mechanical properties and low cost. The main problem of applying carbon steel is its dissolution in acidic solutions. Then, its protection in acidic solutions by different organic compounds has been extensively studied [1-5]. The use of inhibitors is the most economical and practical method to minimize the corrosive attack on metals [6-33]. During the past decade, the corrosion inhibition of carbon steel in acidic solutions by various types of organic inhibitors has attracted much attention [34,35]. There is a continuing effort to find an effective corrosion inhibitor with high inhibition efficiency at very low concentration in the corrosion medium. This is a challenging problem in the steel industry because corrosion over carbon steel surfaces affects long term industrial projects. The performance of the corrosion inhibitors based on organic compounds containing nitrogen, sulphur and oxygen atoms shows promising results [5,23,26]. The inhibitors influence the kinetics of the electrochemical reactions which constitute the corrosion process and thereby modify the metal dissolution in acidic medium. These organic inhibitors act by adsorption on metallic surface changing its electrical double layer structure.

However, the phosphoric acid is widely used in the surface treatment of steel such as chemical and electrolytic polishing or etching, chemical colouring, removal of oxide film, phosphating, passivating, and surface cleaning. So, this acid is a strong acid medium, it shows strong corrosiveness on steel. There is a great need to protect steel materials used in H_3PO_4 solution. Compared with the corrosion inhibition studies of steel in HCl and H_2SO_4 medium, the attention on H_3PO_4 medium is limited'. Up to now, some kinds of organic compounds to have been used as steel corrosion inhibitors in phosphoric acid solution, such as polymers [36], N-heterocyclic compounds [37-41], n-alkyl-quaternary ammonium salt [42], thiosemicarbazide derivatives [43-45] and ruthenium-ligand complex [46]. However, literature reveals that data regarding the use of benzodiazepine derivatives as corrosion inhibitor for steel in H_3PO_4 is very scarce and to the best of our knowledge, 4-(2-oxo-propylidene)-1,5-benzodiazepin-2-one (OPBz) has not been used as a corrosion inhibitor for steel in H3PO4'.
In the present work, the inhibition effect of acetate benzodiazipin derivative on the carbon steel corrosion in 2.0 M H_3PO_4 solution at 303-333K range was studied using electrochemical methods. The adsorption isotherm of inhibitor on steel surface was determined. The kinetic parameters are calculated and discussed.

2. Experimental details

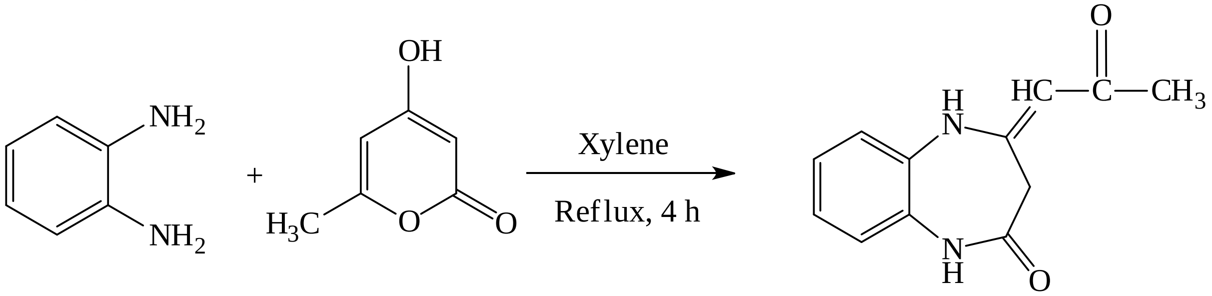
2.1. *Inhibitor*

2.1.1. General method

All chemicals were purchased from Aldrich or Acros (France). The melting point of the studied compound was determined on an automatic electrothermal IA 9200 digital melting point apparatus in capillary tubes. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 WB spectrometer at 300 MHz for solutions in Me_2SO-d_6. The chemical shifts are reported as δ in parts per million (ppm) values with reference to tetramethylsilane (TMS) as internal standard. In addition, the Infrared spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} on a Bruker IFS 66v Fourier transform spectrometer using KBr pellets and the Mass spectrum was recorded on THERMO Electron DSQ II.

2.1.2. Compound synthesis

The 4-(2-oxo-propylidene)-1,5-benzodiazepin-2-one (OPBz) has been synthesized using a method described elsewhere [47], which consists of the reaction of 1,2-diaminobenzene with g-pyrone in o-xylene as solvent (Scheme 1). The identity of the compound was confirmed by 1H and 13C NMR, IR and Mass spectroscopy. So, a mixture of 1,2-diaminobenzene (60 mmol) and □-pyrone (80 mmol) in 80 ml xylene was heated under reflux for 4 hours and the water is removed with a Dean-Stark trap by azeotropic distillation. The obtained mixture was evaporated and purified by column chromatography (silica gel using Chloroforme-ether gradient as eluent, (60-40 %) to give 4-(2-oxo-propylidene)-1,5-benzodiazepin-2-one (OPBz) as a yellow solid (65 % yield), mp 230-232 °C (ethanol)). The ^{1}H RMN (DMSO-d_6): 2.00 (3H,s); 3.00 (2H, s); 5.20 (1H, s); 7.10 (4H, m); IR (KBr) : (O=C=NH) 1680, (O=C-CH_3) 1610, (C=C) 1570 cm^{-1}; SM (m/z) = 216.



Scheme 1: Synthesis of 4-(2-oxo-propylidene)-1,5-benzodiazepin-2-one (OPBz).

2.2. Materials

The steel used in this study is a carbon steel (CS) (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and then remainder iron (Fe). The aggressive solution of 2.0 M H_3PO_4 was prepared by dilution of analytical grade 85 % H_3PO_4 with distilled water. The concentration range of the tested compound was 10^{-3} to10^{-5} M.

2.3. Corrosion tests

2.3.1. Electrochemical impedance spectroscopy

The electrochemical measurements were carried out using Volta lab (Tacussel- Radiometer PGZ 100) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference and auxiliary electrodes were (SCE) and platinum electrodes, respectively. All potentials given in this study were referred to the saturated calomel electrode. The working electrode was immersed in test solution for 30 minutes to a establish steady state open circuit potential (*E*ocp). All electrochemical tests have been performed in aerated solutions at 303 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the *x*-axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation:

$$\eta_z\% = \frac{R_{ct}^{i} - R_{ct}^{\circ}}{R_{ct}^{i}} \times 100 \qquad (1)$$

where, R_{ct}° and R_{ct}^{i} are the charge transfer resistance in absence and in presence of inhibitor, respectively.

2.3.2. Potentiodynamic polarization

The electrochemical behaviour of carbon steel was studied by recording anodic and cathodic potentiodynamic polarization curves. The measurements were performed by changing the electrode potential automatically from -900 mV to -100 mV versus corrosion potential at a scan rate of 1 mV s^{-1}. From the obtained polarization curves, the corrosion current (I_{corr}) was calculated by curve fitting using the equation:

$$I = I_{corr}\left[exp\left(\frac{2.3\Delta E}{\beta_a}\right) - exp\left(\frac{2.3\Delta E}{\beta_c}\right)\right] \qquad (2)$$

where β_a and β_c are the anodic and cathodic Tafel slopes and ΔE is E-E_{corr}.

The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$\eta_{Tafel}\% = \frac{I_{corr}^{\circ} - I_{corr}^{i}}{I_{corr}^{\circ}} \times 100 \qquad (3)$$

where, I_{corr}° and I_{corr}^{i} are the corrosion current density in the absence and presence of inhibitor, respectively.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS)

Figure 1 shows the Nyquist diagrams for carbon steel in 2.0 M H_3PO_4 containing different concentrations of 4-(2-oxo-propylidene)-1,5-benzodiazepin-2-one (OPBz) at 303K. The obtained spectra exhibit one single capacitive loop, which indicates that the charge transfer takes place at electrode/solution interface, and the transfer process controls corrosion reaction and the presence of OPBz doesn't change the steel dissolution mechanism [48]. Noticeably, these impedance diagrams are not perfect semicircles which are related to the frequency dispersion as a result of the roughness and inhomogeneous of electrode surface [49]. Furthermore, it is observed that the impedance response of carbon steel in uninhibited H_3PO_4 solution changes significantly after OPBz addition in the corrosive solution with an increase in its diameter. The electrochemical parameters such as R_{ct}, C_{dl} and η_z (%) are summarized in Table 1. It is noted that the C_{dl} values tend to decrease and the inhibition efficiency increases with inhibitor concentration. This decrease in C_{dl} values can be attributed to a decrease in local dielectric constant and/or an increase in the electrical double layer thickness, suggesting that OPBz acts by adsorption at the carbon steel/solution interface [50, 51]. This situation was the result of an increase in the surface coverage by this inhibitor, which leads to an increase in the inhibition efficiency. In addition, the thickness of the protective layer, δ, was related to C_{dl} value by the following equation:

$$C_{dl} = \frac{\varepsilon_o \varepsilon}{\delta} S \qquad (4)$$

where δ is the protective layer thickness, S is the electrode area, ε_o is the vacuum permittivity of vide and ε is the dielectric constant of the medium.

So, the adsorption of an organic inhibitor on metallic surface involves the replacement of water molecules and/or other ions already adsorbed on the surface. Then, the smaller dielectric constant of organic compounds compared to water as well as the increased of the double layer thickness due to inhibitor adsorption causing a reduce of the interfacial capacitance [52-54]. This provides experimental evidence of adsorption of the OPBz on the carbon steel surface.

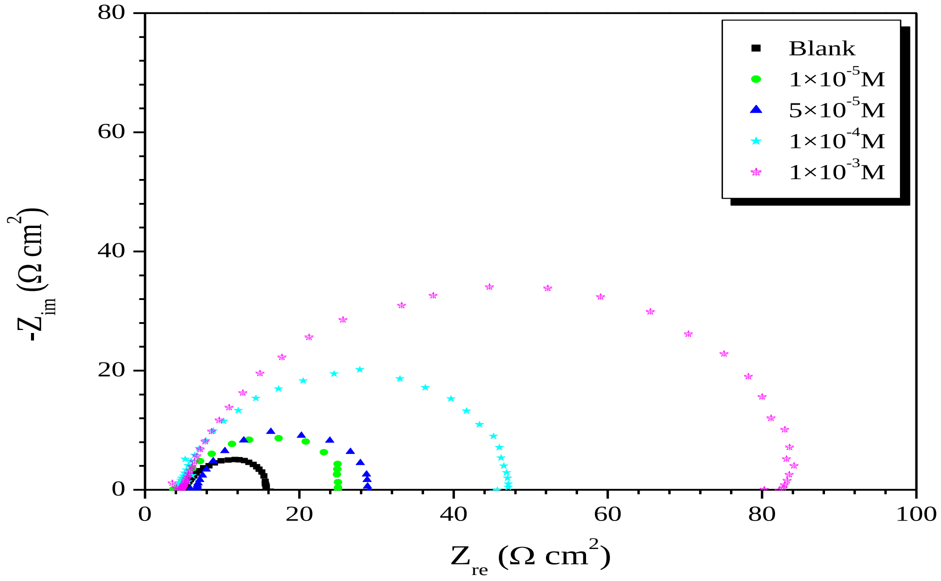


Figure 1: Nyquist plots of carbon steel in 2.0 M H_3PO_4 without and with different concentrations of OPBz at 303 K.

Table 1: Electrochemical impedance parameters and inhibition efficiencies for carbon steel in 2.0 M H_3PO_4 solution without and with OPBz at 303K.

Medium	Conc. (M)	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	η_z (%)
Blank	2.0	11.8	118.0	—
OPBz	1×10^{-3}	80.5	62.5	85.3
	1×10^{-4}	44.0	72.4	73.2
	5×10^{-5}	25.0	80.6	52.8
	1×10^{-5}	19.5	103.4	39.5

3.2. Tafel Polarization Study

3.2.1. Effect of concentration

Figure 2 illustrates the polarization curves of carbon steel in 2.0 M H_3PO_4 solution without and with various concentrations of OPBz at 303K. Their corresponding parameters and inhibition efficiencies (η_{Tafel}) values are summarized in Table 2. From Figure 2, it is clear that both anodic and cathodic Tafel curves shift towards the lower current densities in the presence of OPBz. This phenomenon implies that both anodic metal dissolution and cathodic hydrogen evolution reactions are retarded. Meanwhile, this suppression effect becomes more pronounced with the increasing of OPBz concentration.

According to the literature [55,56], it has been reported that if the displacement in E_{corr} in the presence of inhibitor is more than 85 mV with respect to E_{corr} of the blank, the inhibitor can be recognized as cathodic or anodic- type inhibitor. On the contrary, if the displacement in E_{corr} is less than 85 mV, the inhibitor can be classified as a mixed- type inhibitor. In the present study, the maximum shift is 7 mV and the E_{corr} shifts towards negative values in the presence of OPBz, which indicates that OPBz acts as a mixed-type inhibitor and has more influence on the cathodic polarization plots. The cathodic Tafel slopes (β_c) change remarkably with the presence of OPBz indicating a in the hydrogen evolution mechanism. It is worth noting that the inhibition efficiencies calculated from the EIS measurements show the same trend as that obtained from potentiodynamic polarization measurements.

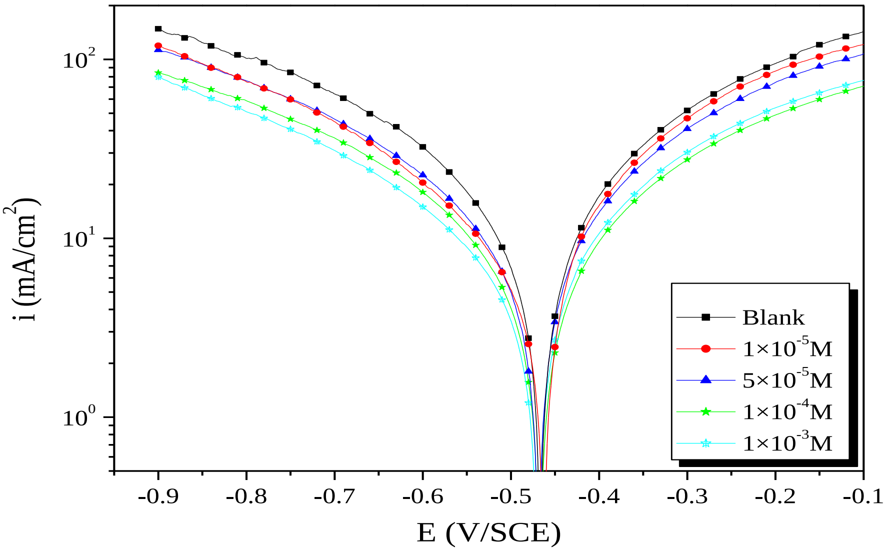


Figure 2: Polarization curves of carbon steel in 2.0 M H_3PO_4 without and with different concentrations of OPBz at 303 K.

Table 2: Electrochemical parameters and inhibition efficiencies for carbon steel in 2.0 M H_3PO_4 in the absence and presence of different concentrations of OPBz at 303 K.

Conc. (M)	$-E_{corr}$ (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} (µA/cm^2)	η_{Tafel} (%)
00	471	170	2169.1	—
1×10^{-3}	464	133	0256.0	88.2
1×10^{-4}	467	140	0501.0	76.9
5×10^{-5}	472	156	0976.0	55.0
1×10^{-5}	474	182	1300.0	40.0

3.2.2. Effect of temperature

Generally, the adsorption phenomenon has been successfully explained by thermodynamic parameters. For this, we have studied the effect of temperature on the corrosion rate of carbon steel in 2.0 H_3PO_4 in the absence and presence of 10^{-3} M of OPBz in the range from 303 K to 333 K using potentiodynamic polarization curves. The obtained results are presented in Figure 3a and b. It is clear that any change observed in the obtained curves with temperature indicating any change in the corrosion process.

The electrochemical parameters were extracted and summarized in Table 3. It is obvious that the I_{corr} values increase with increase of temperature in both solutions and the inhibition efficiencies values decreases. The inhibition efficiency of OPBz reaches a maximum value (88 %) at 303K, upon increasing the temperature, the η_{Tafel} decreased slightly in the presence of OPBz compared to the blank solution. This behavior shows again the physical nature of adsorption of OPBz at the metallic surface in H_3PO_4 solution. However, the activation parameters such as the activation energy, E_a, the enthalpy of activation, ΔH_a, and the entropy of activation, ΔS_a, for carbon steel corrosion in 2.0 M H_3PO_4 without and with 10^{-3} M of OPBz at different temperatures were calculated from an Arrhenius-type plot and the transition state using Equation (5) and (6), respectively [57,58]:

$$I_{corr} = k \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where E_a is the apparent activation corrosion energy, T is the absolute temperature, k is the Arrhenius pre-exponential constant and R is the universal gas constant.

$$I_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{\Delta H_a}{RT}\right) \quad (6)$$

where h is Planck's constant, N is Avogadro's number and ΔS_a and ΔH_a are the entropy and enthalpy of activation, respectively.

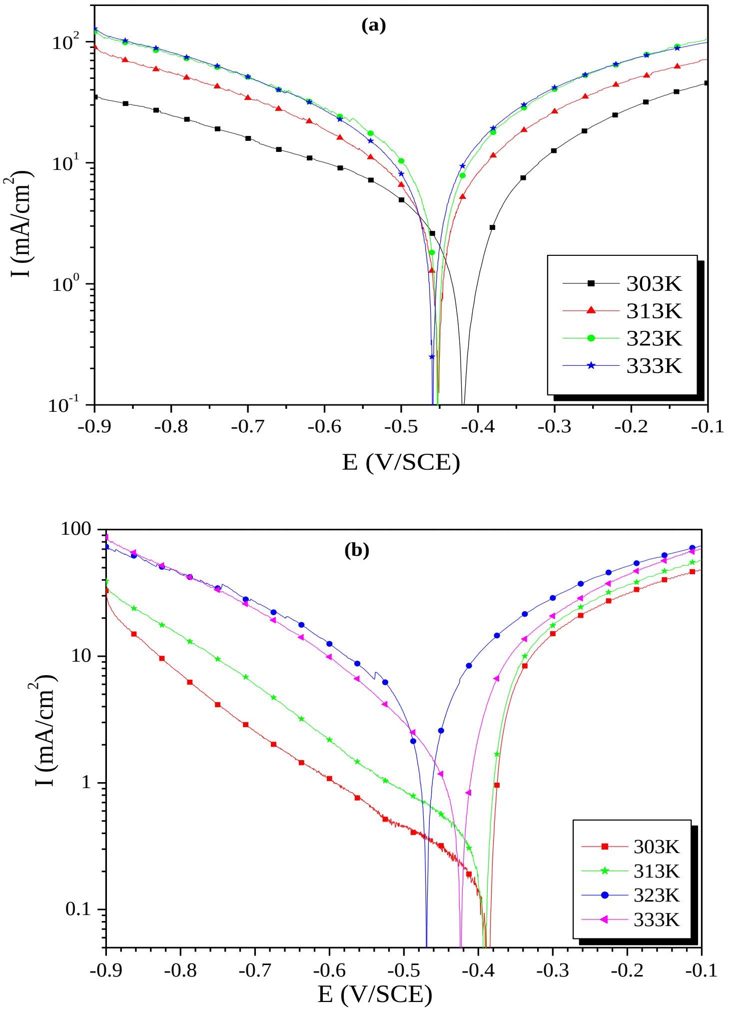


Figure 3: Potentiodynamic polarization curves for carbon steel in 2.0 M H_3PO_4 (a) without Inhibitor and (b) with 10^{-3} M of OPBz at different temperatures.

Table 3: Polarization parameters and the inhibition efficiencies for carbon steel in 2.0 M H_3PO_4 in the absence and presence of 10^{-3} M of OPBz at different temperatures.

Medium	T (K)	$-E_{corr}$ (mV_{SCE})	I_{corr} ($\mu A\ cm^{-2}$)	η_{Tafel} (%)
Blank	303	418	2170	—
	313	452	4910	—
	323	491	6830	—
	333	459	9390	—
OPBz	303	388	250	88
	313	473	2183	70
	323	479	2223	55
	333	471	4706	50

The obtained plots of Ln (I_{corr}) vs. 1000/T and Ln (I_{corr}/T) vs. 1000/T gave a straight lines with slopes of -E_a/R and -ΔH_a/R, respectively. The intercepts were A and [Ln (R/Nh) + (ΔS_a/R)] for the Arrhenius and transition state equations, respectively. Figures 4 and 5 represent the obtained plots in the absence and presence of 10^{-3} M of OPBz. The calculated values are tabulated in Table 4.

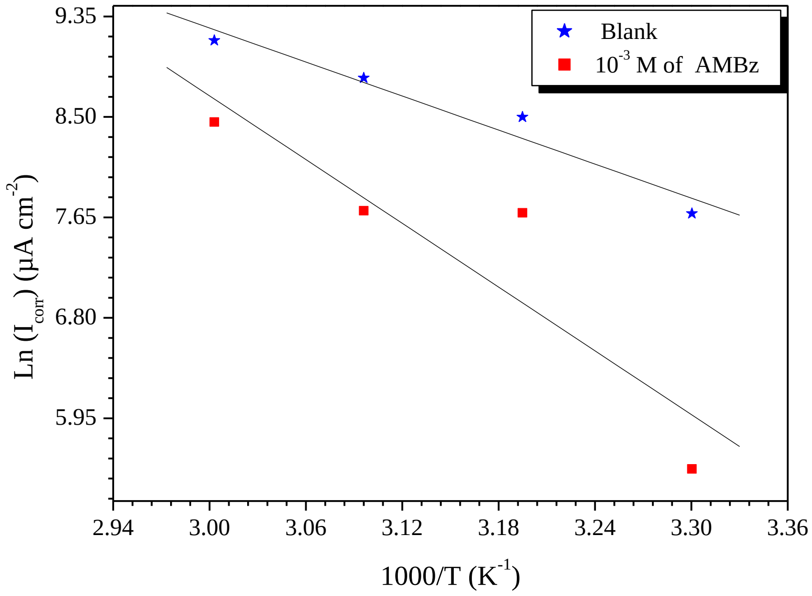


Figure 4: Arrhenius plots of carbon steel in 2.0 M H_3PO_4 without and with 10^{-3} M of OPBz.

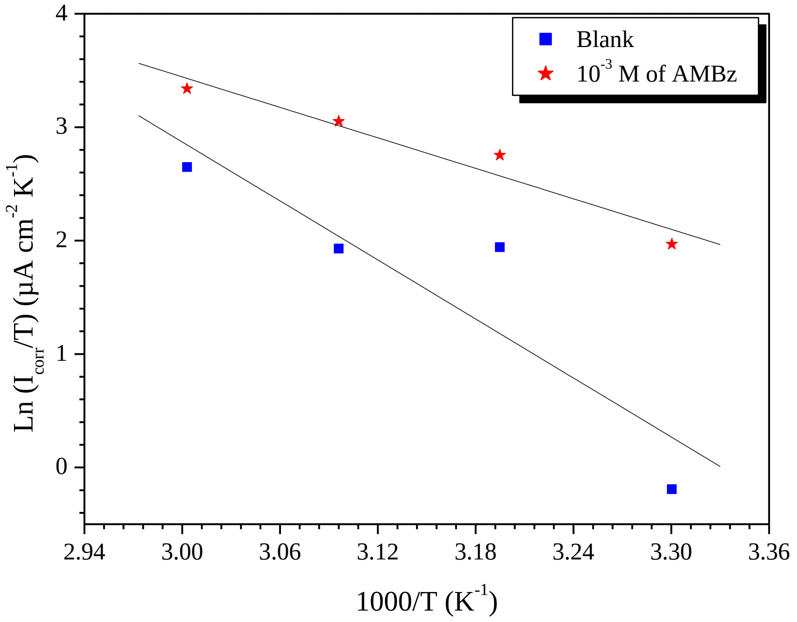


Figure 5: Transition Arrhenius plots of carbon steel in 2.0 M H_3PO_4 without and with 10^{-3} M of OPBz.

Table 4: Activation parameters, E_a, ΔH_a and ΔS_a values of carbon steel dissolution in 2.0 M H_3PO_4 without and with 10^{-3} M of OPBz

Medium	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J mol^{-1} K^{-1})
Blank	39.87	37.23	-57.20
10^{-3} M of OPBz	74.74	72.09	042.61

Inspection of this Table shows that both E_a, ΔH_a values in the presence 10^{-3} M of OPBz are higher than those obtained in the inhibitor-free solution. This observation further supports the proposed physical adsorption mechanism. In addition, the higher values of E_a in inhibited systems compared to the blank have been reported to be indicative of physical adsorption mechanism, while lower values of E_a suggest a chemisorption mechanism [59-61]. On the other hand, the positive sign of ΔH_a reflects the endothermic nature of the carbon steel dissolution process suggesting that the rate dissolution is slow in the presence of inhibitor [62]. This behaviour can be also explained by the result of the replacement process of water molecules by the OPBz molecules adsorption on steel surface [63,64]. Finally, the large negative value of ΔS_a for carbon steel in 2.0 M H_3PO_4 implies that the activated complex is the rate-determining step, rather than the dissociation step. In the presence of OPBz, the ΔS_a value increases indicating an increase in disorder as the reactants are converted to the activated complexes [65].

3.3. Adsorption isotherm

The adsorption isotherm that describes the adsorptive behavior of organic inhibitors is important in order to know the corrosion inhibition mechanism. Basic information dealing with interaction between the inhibitor molecules and the metal surface can be provided by adsorption isotherms. Several adsorption isotherms were attempted to fit the coverage surface degree values (θ) to adsorption isotherms including Frumkin, Temkin, Freundlich and Langmuir isotherms. The θ values for various concentrations of inhibitors in acidic media have been evaluated from the polarization measurements. The best fit was obtained in the case of Langmuir isotherm which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species [66]. The plot of C_{inh}/θ vs. C_{inh} (Figure 6) yields a straight line with correlation coefficient of 0.999 providing that the adsorption of OPBz molecules from 2.0 M H_3PO_4 solution on the carbon steel surface obeys Langmuir adsorption isotherm. This isotherm can be represented as:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (7)$$

where C_{inh} is the inhibitor concentration and K_{ads} is the equilibrium constant for the adsorption-desorption process. The K_{ads} value was found to be 44138.61 M^{-1}. The relatively high value of adsorption equilibrium constant reflects the high adsorption ability of OPBz on carbon steel surface [67].

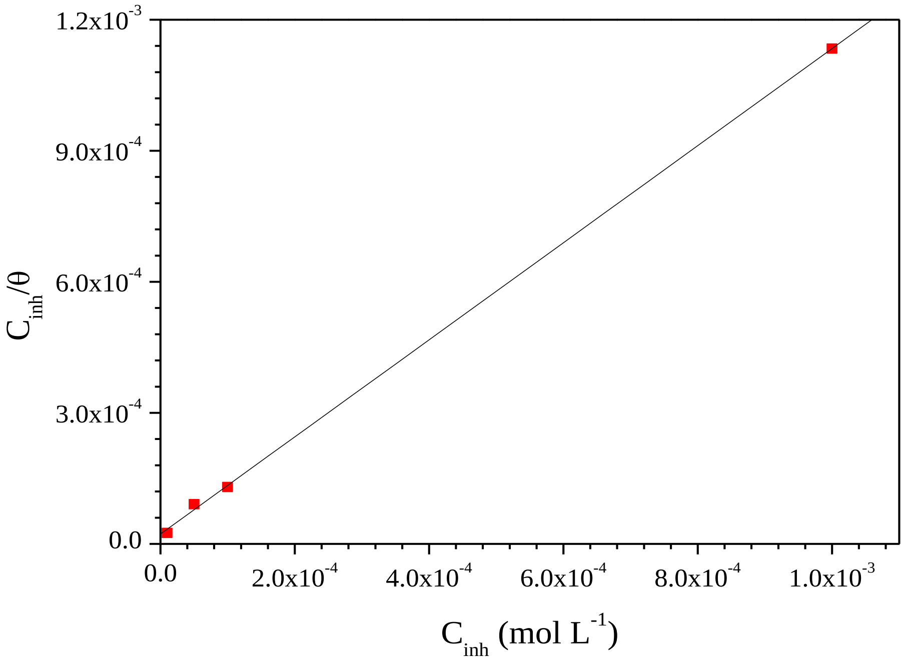


Figure 6: Langmuir adsorption isotherm plots for OPBz at 303K.

The K_{ads} is related to the standard free energy of adsorption, ΔG°_{ads}, by the following equation:

$$K_{ads} = \left(\frac{1}{55.5}\right)\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \tag{8}$$

where R is gas constant and T is absolute temperature and the constant value of 55.5 is the concentration of water in solution in mol L^{-1}.

The ΔG°_{ads} was calculated as -48.24 kJ mol^{-1}. The negative value of ΔG°_{ads} indicates the spontaneity of the adsorption process and the stability of adsorbed layer on the carbon steel surface. It is well known that when the ΔG°_{ads} values in the order of -20 kJ mol^{-1} or lower indicate a physisorption; those of order of -40 kJ mol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [68-70]. On the other hand, the adsorption phenomenon of an organic molecule is not considered only as a purely physical or chemical adsorption phenomenon [71,72]. A wide spectrum of conditions, ranging from the dominance of chemisorption or electrostatic effects, arises from other adsorptions experimental data [73].

Conclusions

The corrosion inhibition of carbon steel in 2.0 M H_3PO_4 solution by OPBz was studied using electrochemical techniques. According to experimental findings, it could be concluded that:

- OPBz shows good inhibition efficiency for carbon steel corrosion in 2.0 M H_3PO_4 and this inhibition depends on its concentration
- The polarization curves showed that the OPBz acts as mixed-type inhibitor.
- OPBz is a good corrosion inhibitor for the carbon steel protection in 2.0 M H_3PO_4 solution..
- EIS plots indicated that R_{ct} values increase and C_{dl} values decrease with inhibitor concentration.
- The adsorption of OPBz on the steel surface from 2.0 M H_3PO_4 solution follows Langmuir adsorption isotherm. The thermodynamic parameters suggest that this inhibitor is strongly adsorbed on the carbon steel surface.

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