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## Corrosion Inhibition of Steel in phosphoric acid by Sulfapyridine: Experimental and Theoretical Studies

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### ABSTRACT

The corrosion inhibition efficiency of Sulfapyridine(SFP) for carbon steel in 2.0 M H<sub>3</sub>PO<sub>4</sub> has been studied using weight loss, polarization, electrochemical and impedance spectroscopy techniques. The results show that SFP is a good inhibitor in 2.0 M H<sub>3</sub>PO<sub>4</sub>. Effects of temperature and acid concentration on inhibitive performance were investigated. Polarization curves reveal that SFP acts as a mixed-type inhibitor. The electrochemical impedance spectroscopy showed that the charge transfer resistance increases and the double layer capacitance decreases on increasing Sulfapyridine concentration. Activation energy of corrosion and other thermodynamic parameters such as standard free energy, standard enthalpy, and standard entropy of the adsorption process revealed better and well-ordered physical adsorption mechanism in the presence of Sulfapyridine. Adsorption isotherms in absence or presence of SFP as inhibitor appropriately fit the Langmuir isotherm. Theoretical investigations have established that the interaction of SFP with the metal steel surface is mainly through the Nitrogen, oxygen atoms, sulphonyl group and the  $\pi$  system of the aromatic ring.

**Keywords:** carbon steel, corrosion, H<sub>3</sub>PO<sub>4</sub>, Sulfapyridine, EIS, Polarization, DFT.

### INTRODUCTION

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals and alloys. Steel has found wide applications in a broad spectrum of industries and machinery; despite its tendency to corrosion. Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is widely used in the production of fertilizers and surface treatment of steel such as chemical and electrolytic polishing or etching, chemical coloring, removal of oxide film, phosphating, passivating, and surface cleaning [1]. The use of inhibitors for the control of corrosion for metals and alloys which are in contact with aggressive environment is an accepted practice. Large numbers of organic compounds were studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency [2-7]. Little work [8-14] appears to have been done on the inhibition of mild steel in phosphoric acid solutions. DFT (density functional theory) methods have become very popular in the last decade due to their accuracy and less time requirement from the computational point of view [15]. Based on the well-known Hohenberg-Kohn theorems [16], DFT focuses on the electron density,  $\rho(r)$ , itself as the carrier of all information in the molecular (or atomic) ground state. Important molecular properties of molecules such as dipole moment,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ,  $\Delta E_{\text{L-H}}$ , etc..., have been correlated with inhibition efficiency of different

inhibitors using DFT[17]. In this paper, the kinetics of the corrosion of carbon steel in phosphoric acid have been studied by potentiodynamic polarization, electrochemical impedance spectroscopy, weightloss, methods and theoretical studies. The action of Sulfapyridine as inhibitor in phosphoric acid medium over a range of acid concentration and solution temperature has also been examined.

## MATERIALS AND METHODS

### Materials

The steel used in this study is a carbon steel (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 the remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use.

### Solutions

The aggressive solutions 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 Sulfapyridine used was  $5 \times 10^{-4}M$  to  $1 \times 10^{-5}M$ .

### Corrosion tests

#### Weight loss

Gravimetric measurements were carried out at definite time interval of 6 h at room temperature using an analytical balance (precision  $\pm 0.1$  mg). The carbon steel specimens used have a rectangular form (length = 1.6 cm, width = 1.6 cm, thickness = 0.07 cm). Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser containing 80 mL of non-de-aerated test solution. After immersion period, the steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighed. Triplicate experiments were performed in each case and the mean value of the weight loss was calculated.

#### Electrochemical impedance spectroscopy

The electrochemical measurements were carried out using Volta lab (Tacussel- Radiometer PGZ 100) potentiostat and controlled by Tacussel corrosion analysis software model (Volta master 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode of surface area of  $1 \text{ cm}^2$ . The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to establish steady state open circuit potential ( $E_{ocp}$ ). After measuring the  $E_{ocp}$ , the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 298 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 100 mHz 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.

#### Potentiodynamic polarization

The electrochemical behaviour of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 2.0 M  $H_3PO_4$  solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from - 800 to -200 mV versus corrosion potential at a scan rate of  $2 \text{ mV} \cdot \text{s}^{-1}$ . The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities ( $I_{corr}$ ).

The present investigation was undertaken to examine the corrosion inhibition capacity of Sulfapyridine in 2.0 M  $H_3PO_4$  solution on carbon steel at 298-328 K using potentiodynamic polarisation (PDP) curves and electrochemical impedance spectroscopy (EIS) methods. The adsorption isotherm of inhibitor on steel surface was determined. Kinetic parameters are calculated and discussed in detail. Figure 1 shows the molecular structure of the Sulfapyridine utilised in this investigation.

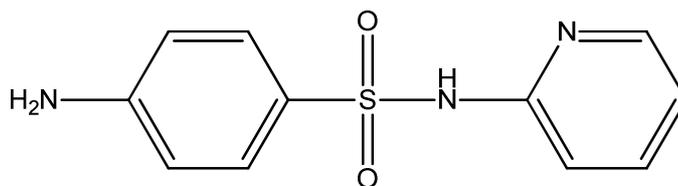


Figure 1: Chemical structure of Sulfapyridine

### Computational procedures

Complete geometrical optimizations of the investigated molecules are performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee-Yang-Parr nonlocal correlation functional (B3LYP) [18-20] with 6-31G(d) basis set is implemented in Gaussian 03 program package [21]. This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations. The geometry structure was optimized under no constraint. The following quantum chemical parameters were calculated from the obtained optimized structure: The highest occupied molecular orbital ( $E_{HOMO}$ ) and the lowest unoccupied molecular orbital ( $E_{LUMO}$ ), the energy difference ( $\Delta E$ ) between  $E_{HOMO}$  and  $E_{LUMO}$ , dipole moment ( $\mu$ ), electron affinity (EA), ionization potential ( $I$ ) and the fraction of electrons transferred ( $\Delta N$ ). Ionization potential ( $I$ ) and electron affinity ( $A$ ) are related [22] in turn to  $E_{HOMO}$  and  $E_{LUMO}$  as follows:

$$I = -E_{HOMO}$$

$$A = -E_{LUMO}$$

The absolute electronegativity  $\chi$  and the absolute hardness  $\eta$  are related [23] in turn to  $I$  and  $A$  as follows:

$$\chi = \frac{I + A}{2} \quad (1)$$

$$\eta = \frac{I - A}{2} \quad (2)$$

The global electrophilicity index was introduced by Parr [24] and is given by:

$$\omega = \frac{\chi^2}{2\eta} \quad (3)$$

The number of transferred electrons ( $\Delta N$ ) was also calculated depending on the quantum chemical method [25, 26] by using the equation;

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (4)$$

Where  $\chi_{Fe}$  and  $\chi_{inh}$  denote the absolute electronegativity of iron and inhibitor molecule  $\eta_{Fe}$  and  $\eta_{inh}$  denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of  $\chi_{Fe} = 7.0$  eV and  $\eta_{Fe} = 0$ , for calculating the number of electron transferred.

## RESULTS AND DISCUSSION

### Effect of concentration inhibitor

#### Weight loss

The corrosion rate ( $A$ ) of carbon steel specimens after 2 h exposure to 2.0 M  $H_3PO_4$  solution with and without the addition of various concentrations of the investigated inhibitor was calculated and the obtained data are listed in Table 1. The variation of  $A$  with inhibitor concentrations is shown in Fig. 2. The corrosion rate,  $A$  ( $mg\ cm^{-2}\ h^{-1}$ ), surface coverage ( $\theta$ ) and inhibition efficiency  $\eta_w$  of each concentration were calculated using the following equations [27]:

$$A = \frac{\Delta W}{St} \quad (5)$$

$$\theta = \frac{A_{uninh} - A_{inh}}{A_{uninh}} \quad (6)$$

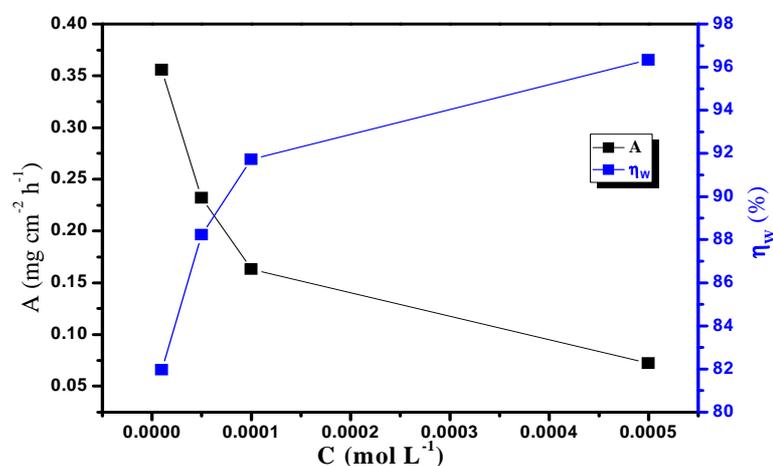
$$\eta_w = \left( \frac{A_{\text{uninh}} - A_{\text{inh}}}{A_{\text{uninh}}} \right) \times 100 \quad (7)$$

Where  $\Delta W$  is the average weight loss (mg),  $S$  is the surface area of specimens ( $\text{cm}^2$ ), and  $t$  is the immersion time (h),  $A_{\text{uninh}}$  and  $A_{\text{inh}}$  are corrosion rates in the absence and presence of inhibitor, respectively.

**Table1.** Effect of SFP concentration on corrosion data of carbon steel in 2.0 M  $\text{H}_3\text{PO}_4$

Inhibitor	Conc. (M)	A ( $\text{mg cm}^{-2} \text{h}^{-1}$ )	$\eta_w$ (%)	( $\theta$ )
Blank	2.0	1.972	-	-
SFP	$5 \times 10^{-4}$	0.0722	96.34	0.9634
	$1 \times 10^{-4}$	0.1631	91.73	0.9173
	$5 \times 10^{-5}$	0.2321	88.23	0.8823
	$1 \times 10^{-5}$	0.3557	81.96	0.8196

From the Table1 and the Fig.2, it is clear that increase of inhibitor concentration caused a decrease in the weight loss as well as corrosion rate of mild steel and, increasing the efficiency of inhibition to reach the maximum value of **96.34%** at the highest concentration of  $5 \times 10^{-4}$  M. This shows that the molecule of SFP may be adsorbed on the metal surface to cover the active sites on the electrode surface.



**Figure 2.** Variation of inhibition efficiency and corrosion rate in 2.0 M  $\text{H}_3\text{PO}_4$  on mild steel surface without and with different concentrations of SFP

### Electrochemical impedance spectroscopy

Nyquist representation of the EIS study of mild steel in 2.0 M  $\text{H}_3\text{PO}_4$  in absence and presence of different concentration of SFP were presented in figure 3. The large capacitive loop attributed to the adsorption of the inhibitor molecule [28]. The simple equivalent Randle circuit for studies is shown in Fig. 3, where  $R_s$  represents the solution and corrosion product film; the parallel combination of resistor,  $R_{ct}$  and capacitor  $C_{dl}$  represents the corroding interface. The existence of single semi circle showed the single charge transfer process. Depression from the perfect semi circle is due to the inhomogeneous nature of the metal surface arising from the surface roughness or the interfacial phenomenon [29]. The increase in  $R_{ct}$  values due to the addition of inhibitor in comparison to the absence of inhibitor is attributed to the formation of protective film on the metal/solution interface. These observations suggest that SFP molecules function by adsorption at metal surface thereby causing the decrease in  $C_{dl}$  values and increase in  $R_{ct}$  values [30].

The electrochemical parameters, including  $R_{ct}$ ,  $Y_0$  and  $n$ , obtained from fitting the recorded EIS data using the electrochemical circuit of Figure 4 are listed in Table 2. The impedance of the CPE is expressed as follows [51].

$$Z_{CPE} = \frac{1}{Y_0 (j\omega)^n} \quad (8)$$

Where  $Y_0$  is the CPE constant,  $n$  is the phase shift which can be explained as a degree of surface inhomogeneity,  $j$  is the imaginary unit and  $\omega$  is the angular frequency. Depending on the values of  $n$ , CPE can represent resistance

(n=0), capacitance (n=1), inductance (n= -1) and Warburg impedance (n=0.5). The values of the interfacial capacitance  $C_{dl}$  can be calculated from CPE parameter values  $Y_0$  and n using the expression [32]:

$$C_{dl} = \frac{Y_0 \omega^{n-1}}{\sin(n\pi / 2)} \tag{9}$$

Decrease in  $C_{dl}$ , which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecules act by adsorption at the metal/solution interface [33].

The  $R_{ct}$  values were used to calculate the inhibition efficiency,  $\eta_z(\%)$ , (listed in Table 2), using the following equation:

$$\eta_z \% = \frac{R_{ct}^i - R_{ct}^o}{R_{ct}^i} \times 100 \tag{10}$$

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

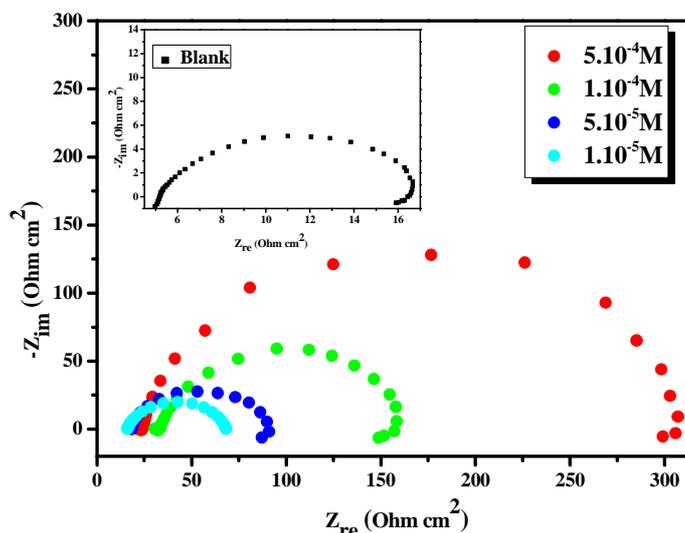


Figure3. Nyquist diagrams of carbon steel with different concentrations of SFP at 298K

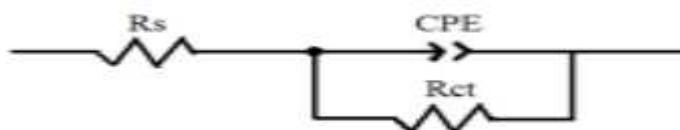


Figure4. Equivalent electrical circuit corresponding to the corrosion process on the carbon steel in phosphoric acid

Table2. Electrochemical Impedance parameters for corrosion of carbon steel in acid medium at various contents of SFP

Inhibitor	Concentration (M)	$R_t$ ( $\Omega \text{ cm}^2$ )	$Y_0 \times 10^{-5}$ ( $\text{s}^n \Omega^{-1} \text{ cm}^{-2}$ )	n	$C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ )	$\eta_z$ (%)
Blank	2.0	14	21.024	0.88	94.96	—
	$5 \times 10^{-4}$	299.2	1.2542	0.92	07.72	94.8
SFP	$1 \times 10^{-4}$	149	3.0945	0.91	18.18	90.6
	$5 \times 10^{-5}$	67.1	5.7878	0.88	27.15	79.1
	$1 \times 10^{-5}$	52.3	9.5927	0.83	32.43	73.2

### Polarization curves

The potentiodynamic polarization measurements were carried out to study the kinetics of the cathodic and anodic reactions. Figure 5 shows the results of the effect of Sulfapyridine inhibitor on the cathodic as well as anodic polarization curves of mild steel in 2.0 M  $\text{H}_3\text{PO}_4$  respectively. It is evident from the figure that both reactions were suppressed with the addition of this inhibitor. This suggests that Sulfapyridine reduced the anodic dissolution reactions as well as retarded the hydrogen evolution reactions on the cathodic sites. Electrochemical corrosion kinetic parameters namely corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ) and cathodic Tafel slope ( $\beta_c$ ) obtained from the extrapolation of the polarization curves are listed in Table 3.

The  $I_{\text{corr}}$  values were used to calculate the inhibition efficiency,  $\eta_{\text{IE}}(\%)$ , (listed in Table 3), using the following equation [34]:

$$\eta_{\text{IE}} \% = \frac{I_{\text{corr}} - I_{\text{corr}(i)}}{I_{\text{corr}}} \times 100 \quad (11)$$

Where,  $I_{\text{corr}}$  and  $I_{\text{corr}(i)}$  are the corrosion current density in absence and presence of inhibitor, respectively.

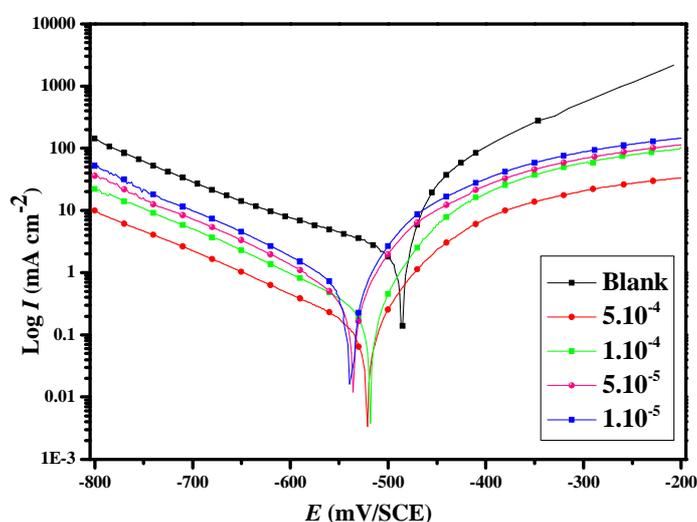


Figure5. Potentiodynamic polarization curves of carbon steel in 2.0 M  $\text{H}_3\text{PO}_4$  in the presence of different concentrations of SFP

$E_{\text{corr}}$  values was shifted towards less negative potential which is a necessary to quote the inhibitive action of inhibitor and to classify an inhibitor into an anodic, a cathodic, or mixed type. It has been reported that [35], an inhibitor can be classified as an anodic or a cathodic-type inhibitor on the basis of magnitude of shift in  $E_{\text{corr}}$  value. If displacement in  $E_{\text{corr}}$  is greater than 85 mV, towards anode or cathode with reference to blank, then an inhibitor is categorized as either anodic or cathodic type inhibitor, respectively. Otherwise an inhibitor is treated as mixed type. In our study, maximum displacement in  $E_{\text{corr}}$  value was around 64 mV indicating Sulfapyridine area mixed type inhibitor, in 2.0 M  $\text{H}_3\text{PO}_4$ . Fig. 5 represents the polarisation curves of C38 steel in 2.0 M  $\text{H}_3\text{PO}_4$  without and with the different inhibitors in concentrations of  $5 \times 10^{-4}\text{M}$  -  $1 \times 10^{-5}\text{M}$  by weight at 298 K. It is clear from Fig. 5 that the cathodic current densities decrease with increasing the concentrations of the inhibitors; this indicates that these compounds are adsorbed on the metal surface and hence inhibition occurs. Thus, the addition of this inhibitor hindered the acid attack on the C38 steel electrode. The parallel cathodic Tafel curves in Fig. 5 reveal that the hydrogen evolution is activation-controlled and the hydrogen evolution reaction (reduction mechanism) is not affected by the presence of the inhibitors [36].

**Table3. Electrochemical parameters of carbon steel at various concentrations of SFP in 2.0 M H<sub>3</sub>PO<sub>4</sub> and corresponding inhibition efficiency**

Inhibitor	Concentration (M)	E <sub>corr</sub> vs. SCE (mV)	-β <sub>c</sub> (mV dec <sup>-1</sup> )	I <sub>corr</sub> (μA cm <sup>-2</sup> )	η <sub>Tafel</sub> (%)
<b>Blank</b>	2.0	-488	135	2718	—
	5 × 10 <sup>-4</sup>	-526	139	125	95.4
<b>(SFP)</b>	1 × 10 <sup>-4</sup>	-541	136	241	91.2
	5 × 10 <sup>-5</sup>	-548	142	483	82.3
	1 × 10 <sup>-5</sup>	-552	149	618	77.3

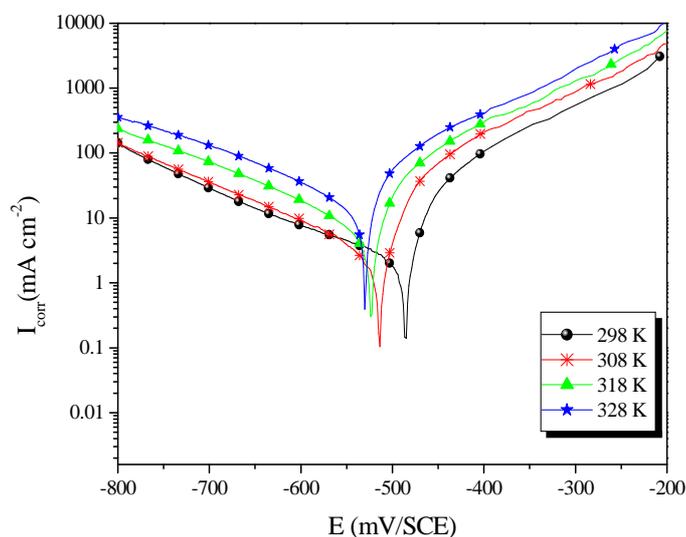
The results in Table 3 show that the inhibition efficiency increased, while the corrosion current density decreased with the addition of inhibitors. This may be due to the adsorption of inhibitors on C38 steel/acid interface. The lowest current density value (125 μA cm<sup>-2</sup>) and best inhibition efficiency was obtained for **SFP** at 5 × 10<sup>-4</sup>. The results in Table 3 indicated that the increase of inhibition efficiency with concentration might be attributed to the formation of the barrier film which prevented acid medium from attacking the metal surface.

### Effect of temperature

Being given that the temperature is one of the factors that may affect the behavior of a material in a corrosive environment, and can also modify the metal-inhibitor interaction, it is essential to study the effect of this factor on the protection rates, as well to determine the mechanism of inhibition, that for calculating the activation energies of the corrosion process.

The study of the influence of temperature on the rate of corrosion inhibition of C38 steel by our inhibitor were performed at temperatures 298, 308, 318, and 328K in the absence and in the presence of inhibitor at 5 × 10<sup>-4</sup>M for 0.5h immersion by potentiodynamic polarization (Figs.6 and 7).

The inhibition efficiencies are found to decrease with increasing the solution temperature from 298K to 328 K. This behaviour can be interpreted on the basis that the increase in temperature results in desorption of the inhibitor molecules from the surface of carbon steel. Table 4 shows that the current densities increased with increasing temperature both in uninhibited and inhibited solutions. The current density increases more rapidly with temperature in the absence of the inhibitor. These results confirm that Sulfapyridine acts as an efficient inhibitor for carbon steel in 2.0 M H<sub>3</sub>PO<sub>4</sub> in the range of temperature studied.

**Figure6. Potentiodynamic polarisation curves of carbon steel in 2.0M H<sub>3</sub>PO<sub>4</sub> at different temperatures**

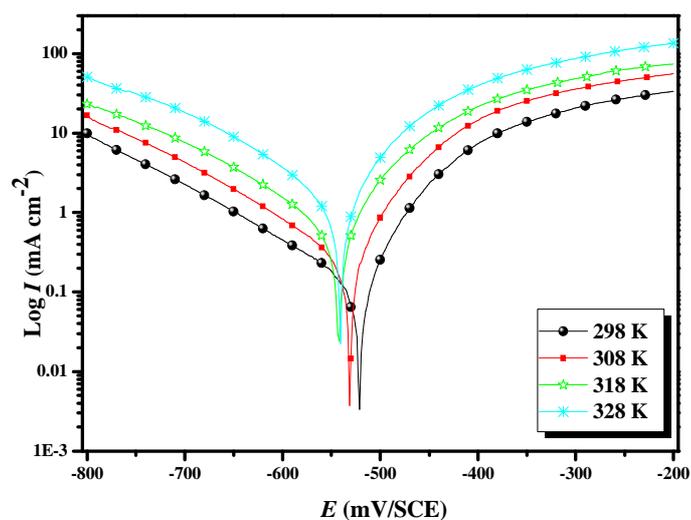


Figure7. Potentiodynamic polarization curves of carbon steel in 2M H<sub>3</sub>PO<sub>4</sub> in the presence 5×10<sup>-4</sup>M of SFP at different temperatures

Table4. Various corrosion parameters for carbon steel in 2M H<sub>3</sub>PO<sub>4</sub> in absence and presence of optimum concentration of SFP at different temperatures

Inhibitor	Temperature K	E <sub>corr</sub> vs. SCE(mV)	-β <sub>c</sub> (mV dec <sup>-1</sup> )	i <sub>corr</sub> (μA cm <sup>-2</sup> )	η <sub>Tafel</sub> (%)
Blank	298	-488	135	2718	—
	308	-532	137	4220	—
	318	-523	132	6610	—
	328	-514	139	11890	—
5 × 10 <sup>-4</sup> M (SFP)	298	-526	139	125	95.4
	308	-537	146	308	92.7
	318	-548	143	648	90.2
	328	-546	146	1593	86.6

The activation parameters were calculated from the Arrhenius-type plot according to equation:

$$I_{corr} = k \exp\left(-\frac{E_a}{RT}\right) \quad (12)$$

Where E<sub>a</sub> is the apparent activation corrosion energy, R is the universal gas constant and k is the Arrhenius pre-exponential constant.

Arrhenius plots for the corrosion density of carbon steel in the case of SFP are given in Fig. 8. Values of apparent activation energy of corrosion (E<sub>a</sub>) for carbon steel in 2.0 M H<sub>3</sub>PO<sub>4</sub> with the absence and presence of Sulfapyridine were determined from the slope of Ln (I<sub>corr</sub>) versus 1/T plots and shown in Table 5.

According to the report in literature [37, 38], higher value of E<sub>a</sub> was considered as physical adsorption that occurred in the first stage. Because the electrochemical corrosion is relevant to heterogeneous reactions, the preexponential factor A in the Arrhenius equation is related to the number of active centers. There are two possibilities about these active centers with different E<sub>a</sub> on the metal surface: (1) the activation energy in the presence of inhibitors is lower than that of pure acidic medium, namely E<sub>a</sub>(-inh) < E<sub>a</sub>(H<sub>3</sub>PO<sub>4</sub>), which suggests a smaller number of more active sites remain uncovered in the corrosion process; (2) the activation energy in the presence of inhibitor is higher than that of pure acidic medium, E<sub>a</sub>(inh) > E<sub>a</sub>(H<sub>3</sub>PO<sub>4</sub>), which represents the inhibitor adsorbed on most active adsorption sites (having the lowest energy) and the corrosion takes place chiefly on the active sites (having higher energy).

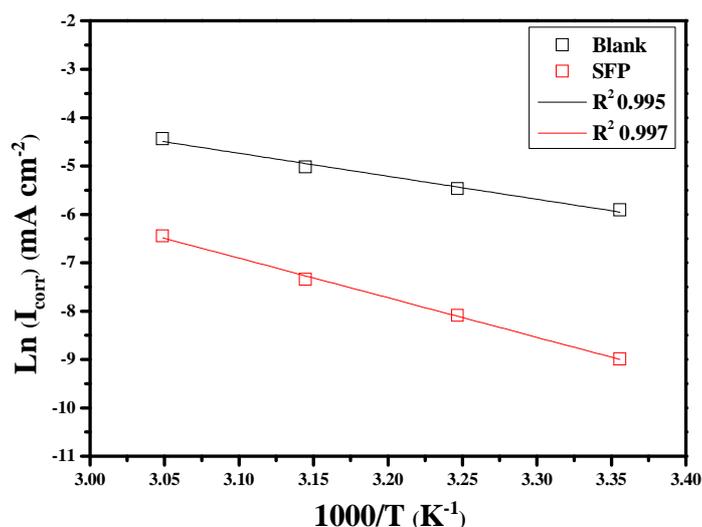


Figure8. Arrhenius plots of carbon steel in 2.0 M H<sub>3</sub>PO<sub>4</sub> with and without 5 × 10<sup>-4</sup>M of SFP

Activation parameters like enthalpy ( $\Delta H_a$ ) and entropy ( $\Delta S_a$ ) for the dissolution of carbon steel in 2.0 M H<sub>3</sub>PO<sub>4</sub> in the absence and presence of 5 × 10<sup>-4</sup>MSFP were calculated from the transition state equation:

$$i_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (13)$$

Where  $h$  is Planck's constant,  $N$  is the Avogadro number,  $R$  is the universal gas constant,  $\Delta H_a$  is the enthalpy of activation and  $\Delta S_a$  is the entropy of activation.

Fig. 9 shows that the Arrhenius plots of  $\ln(i_{corr}/T)$  versus  $1/T$  gave straight lines with slope ( $-\Delta H_a/R$ ) and intercept ( $\ln R/Nh + \Delta S_a/R$ ) from where  $\Delta H_a$  and  $\Delta S_a$  values were calculated. The activation parameters are given in Table 5.

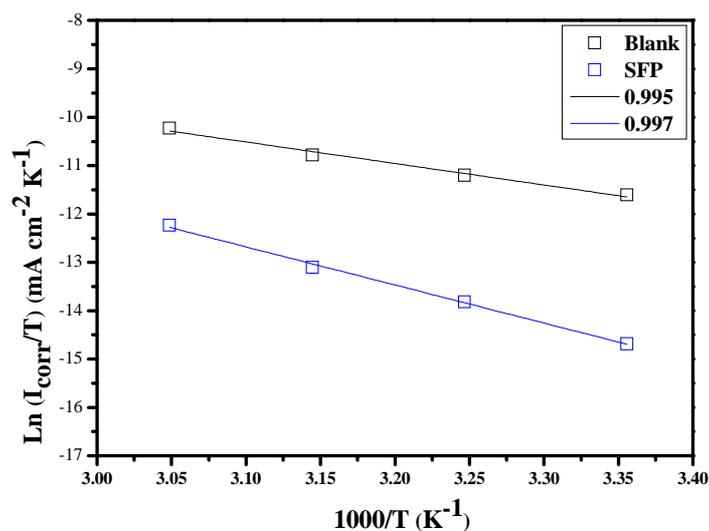


Figure9. Arrhenius plots of carbon steel in 2.0 M H<sub>3</sub>PO<sub>4</sub> with and without 5 × 10<sup>-4</sup>M of SFP

**Table 5.** The values of activation parameters  $E_a$ ,  $\Delta H_a$  and  $\Delta S_a$  for carbon steel in 2.0 M  $H_3PO_4$  in the absence and presence of  $5 \times 10^{-4}$  M of SFP

Concentration (M)	$E_a$ ( $kJ\ mol^{-1}$ )	$\Delta H_a$ ( $kJ\ mol^{-1}$ )	$\Delta S_a$ ( $J\ mol^{-1}\ K^{-1}$ )	$E_a - \Delta H_a$ ( $kJ\ mol^{-1}$ )
Blank	39.50	36.91	-112.98	2.59
$5 \times 10^{-4}$ M SFP	68.05	65.45	-100.06	2.60

In this study the values of  $E_a$  obtained from the slopes of these straight lines are recorded in Table 5. The values of  $E_a$  were higher for inhibited solutions indicating physical adsorption of the inhibitor on the metal surface [39, 40]. However, this energy increases with the addition of the Sulfapyridine compounds into molar solution of phosphoric acid, which shows a change in the mechanism of transition metal in solution. However, several authors [47-46] showed that the increase in  $E_a$  may often be interpreted by the formation of an adsorption film by a physical mechanism (electrostatic). The values of  $E_a$  and  $\Delta H_a$  were increased in the presence of inhibitors, suggesting that the energy barrier of the corrosion reaction increases, meaning that the dissolution of the steel is difficult [44]. According Gomma *et al* [45], the activation energy is much higher than the inhibitor is more effective. However, the positive sign of the endothermic enthalpy reflects the nature of the dissolution of the steel. We note that the variation of the activation energy  $E_a$  and the enthalpy of  $\Delta H_a$  vary in the same way with the concentration of inhibitor, which satisfies the relationship between  $E_a$  and thermodynamics as  $\Delta H_a$  [47]:  $E_a - \Delta H_a = RT$ . The large negative values of entropies ( $\Delta S_a$ ) from SFP imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [48].

#### Adsorption isotherm and standard adsorption free energy

The inhibition of corrosion of metals by organic compounds is explained by their adsorption. The latter is described by two main types of adsorption, namely physical adsorption and chemical adsorption. It depends on the charge of the metal, the nature of the chemical structure of the organic product and the type of electrolyte. The presence of a transition metal, having orbital "d" vacant, and a molecule having centers that facilitates electron rich adsorption [49,50].

The adsorption isotherm can be determined if the mode of action of the inhibitor is mainly due to adsorption on the metal surface. And the type of these isotherms can provide additional information regarding the inhibitory properties of the compounds tested. However, if we assume that the adsorption of our inhibitors adsorption isotherm follows Langmuir, the rate of surface coverage ( $\theta$ ) for different concentrations in acidic medium is evaluated by the method of weight loss according to the report  $E_w$  (%) / 100 and using the following equation [51]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (14)$$

Where  $C_{inh}$  is the concentration of inhibitor and  $K_{ads}$  the adsorptive equilibrium constant.

Figure 10 shows the curves of the variation of  $C_{inh} / \theta$  according to the concentration  $C_{inh}$  for the Sulfapyridine compound. The linearity of these curves indicates that the adsorption of our inhibitors on the surface of C38 steel in 2.0 M  $H_3PO_4$ , is according to the Langmuir isotherm model checking equation (14). The validity of this approach is confirmed by the strong correlation ( $R^2 = 0.999$  for the compound SFP).

The values of  $K_{ads}$  obtained from the reciprocal of intercept of Langmuir isotherm line are listed in Table 6, together with the values of the Gibbs free energy of adsorption  $\Delta G_{ads}^\circ$  calculated from the equation:

$$K_{ads} = \left(\frac{1}{55.5}\right) \exp\left(-\frac{\Delta G_{ads}^\circ}{RT}\right) \quad (15)$$

Where R is gas constant and T is absolute temperature of experiment and the constant value of 55.5 is the concentration of water in solution in  $mol\ dm^{-3}$ .

The high values of adsorption equilibrium constants  $K_{ads}$  correspondent's Sulfapyridine compound to reflect the high adsorption capacity of these inhibitors on the surface of C38 steel in acidic 2.0 M  $H_3PO_4$ . This suggests that this inhibitor can best recoveries, where it's most effective protection against corrosion.

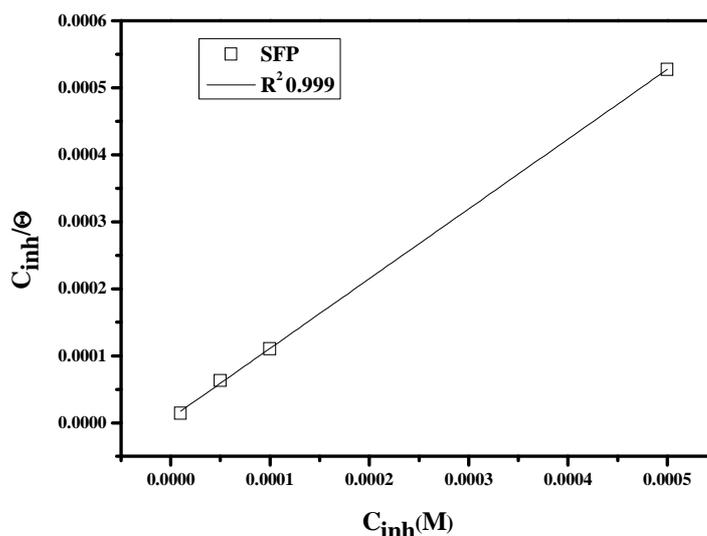


Figure10. Adsorption isotherm according to Langmuir's model derived from EIS measurement

Table5. Thermodynamic parameters for the adsorption of SFP in 2.0 M  $H_3PO_4$  on the carbon steel at 298K.

Inhibitor	Slope	$K_{ads}(M^{-1})$	$\Delta G^*_{ads}(kJ/mol)$
SFP	1.04	142603.51	39.35

The negative values of the standard free energy of adsorption indicates a spontaneous adsorption of molecules on the surface of our C38 steel and also the strong interaction between the inhibitors molecules and the metal surface [52,53]. In general, the standard values of free energy of  $-20 \text{ kJ mol}^{-1}$  or less negative are associated with an electrostatic interaction between the charged molecules and charged metal surface (physical adsorption), those from  $-40 \text{ kJ mol}^{-1}$  or more negative involves a load sharing or transfer inhibitor molecules to the metal surface to form a coordinate covalent bond (chemisorption) [54-56]. The values of  $\Delta G^*_{ads}$  in our measurements (in Table 4) is  $-39.35 \text{ kJ mol}^{-1}$  for **SFP**, it is suggested that the adsorption of this **SFP** involves two types of interactions: chemisorption and physisorption [57].

### Theoretical parameters predicating

Quantum chemical methods and molecular modeling techniques enable the definition of a large number of molecular quantities characterizing the reactivity, shape, and binding properties of a complete molecule as well as of molecular fragments and substituent's. The geometry of the inhibitor as well as the nature of its frontier molecular orbitals, namely, the HOMO and LUMO is involved in the activity properties of the inhibitors. Therefore, in this study, quantum chemical calculations were performed to investigate the relationship between molecular structure of this compound and their inhibition effect. The optimized molecular structure and the frontier molecule orbital density distribution of the studied molecule are shown in Fig. 11, and the calculated quantum chemical parameters  $E_{HOMO}$ ,  $E_{LUMO}$ ,  $\Delta E$  ( $E_{LUMO} - E_{HOMO}$ ), dipole moment ( $\mu$ ), number of transferred electrons ( $\Delta N$ ), and total energy (TE) are given in Table 6.

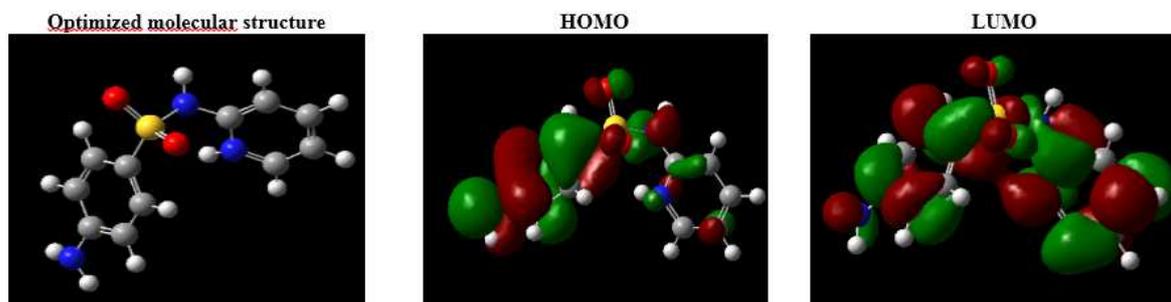


Figure 11. The optimized molecular structure and frontier molecular orbital density distributions of SFP

**Table 6.** Quantum chemical parameters for SFP calculated using B3LYP/6-31G (d,p)

Molecular parameters	SFP
$E_{\text{HOMO}}$ (eV)	-3.3567983
$E_{\text{LUMO}}$ (eV)	-0.94505192
$\Delta E_{\text{gap}}$ (eV)	2.41174638
$\mu$ (debye)	7.5398
I (eV)	3.3567983
A (eV)	0.94505192
$\chi$ (eV)	2.15092511
$\eta$ (eV)	1.20587319
$\omega$	2.7894734
$\Delta N$	2.0106073
TE (a.u.)	-1139.39

Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms [58, 59]. Terms involving the frontier MO could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference [58]. It has been reported in the literature that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied d orbital of the metal, and the higher the corrosion inhibition efficiency. In addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the LUMO–HOMO energy gap decreased and the efficiency of inhibitor improved [60]. For the dipole moment ( $\mu$ ), higher value (7.5398D) will favor a strong interaction of inhibitor molecules to the metal surface. The number of transferred electrons depends strongly on what the actual quantum chemical method employed for computation. Furthermore, the expression “number of transferred electrons” is the wording “electron-donating ability”, which does not imply that the figures of  $\Delta N$  actually indicate the number of electrons leaving the donor and entering the acceptor molecule. The value of electron-donating ability ( $\Delta N$ ) was calculated and its value is given in **Table 6**. If  $\Delta N < 3.6$  (electron), the inhibition efficiency increases with increasing value of  $\Delta N$ , while it decreased if  $\Delta N > 3.6$  (electron) [61]. In present contribution, **SFP** is the donor of electrons, and the iron surface atom was the acceptor. The **SFP** was bound to the mild steel surface, and thus formed inhibition adsorption layer against corrosion at carbon steel/hydrochloric acid solution interface.

## CONCLUSION

All the measurements showed that the **SFP** has excellent inhibition properties against the mild steel corrosion in phosphoric acid solution. Inhibition efficiency of this inhibitor decreases with increase in temperature and further it leads to an increase in activation energy. The inhibitor follows the Langmuir adsorption isotherm in the process of adsorption. EIS measurements also indicates that the inhibitor performance increase due to the adsorption of molecule on the metal surface. Potentiodynamic polarization measurements showed that the inhibitor acts as mixed type of inhibitor. The inhibitor showed maximum inhibition efficiency at  $5 \times 10^{-4}$ M concentration of the studied inhibitor. The inhibition efficiencies determined by EIS, potentiodynamic polarization and weight loss studies are in good agreement. Theoretical calculations provide good support to experimental results.

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