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Study of the Thermodynamic Quantities of Adsorption and Activation of Piroxicam in Copper Corrosion in a Nitric Acid Environment

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Abstract

The objective of this work is to assess the inhibitory efficacy of the piroxicam molecule on copper corrosion in a 1M nitric acid medium using the mass loss technique (gravimetry). The inhibition efficiency, represented as IE (%), increases with higher concentrations and temperatures. Various adsorption isotherm models (Langmuir, El-Awady, Freundlich, and Temkin) were employed to describe the interactions between the molecule and metallic copper. The Dubinin-Radushkevich isotherm, along with the Adejo-Ekwenchi isotherm, was utilized to identify the types of adsorption. Additionally, the thermodynamic adsorption and activation functions were determined and analyzed.

1. Introduction

Copper [1, 2] is one of the most widely used metals in industry due to its mechanical, thermal and electrical conductivity. However, in contact with aggressive media, in particular acidic media, the copper dissolves (corrosion) [3, 4], which has prompted many

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researchers to take an interest in the inhibition of copper corrosion.

Nowadays [5, 6], the use of adsorption inhibitors is much encouraged due to non-toxicity. Recently, drugs such as atenolol, bisoprolol and tenoxicam have been used as inhibitors to fight metal corrosion in an acid environment [7-10]. Medicines may therefore be a better choice because they are available, inexpensive and non-toxic. The main objective of this work is to study the behavior of piroxicam with respect to the corrosion of copper in a 1M nitric acid medium.

2. Material and Methods

2.1. Copper specimens

The copper samples were in the form of a rod 10 mm long and 2 mm in diameter. It is a commercial copper of 98% purity.

Piroxicam: Piroxicam is a drug molecule used for its anti-inflammatory properties. It is used for the treatment of pain associated with rheumatoid arthritis and as a second-line treatment for osteoarthritis. It is marketed under the following names: Brexidol or Durapirox, molecular weight M = 331.348 g.mol^{-1}.

Figure 1 shows the molecular structure of piroxicam.

$C_{15}H_{13}N_3O_4S$

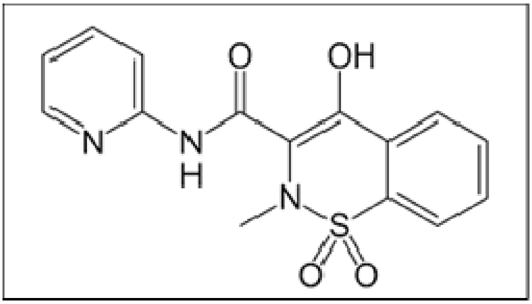

Figure 1. Molecular structure of piroxicam.

2.2. Solution

An analytical grade 65% nitric acid solution from Merck was used to prepare the aqueous corrosive solution. The solution was prepared by diluting the commercial nitric acid solution with bi-distilled water. The blank was a 1 M HNO3 solution. The piroxicam solutions prepared are of concentrations 0.01 mM; 0.05 mM; 0.1 mM; 0.5mM.

2.3. Mass loss method

The mass loss method [11-13] is one of the most widely used methods for evaluating corrosion inhibition of metals due to its simplicity and reliability of measurements. Mass loss measurements were made by total immersion of the pre-weighed copper sample in 100ml capacity beakers containing 50ml of the test solution maintained at a temperature of (298K to 323K). The samples were collected one hour later and rinsed thoroughly with distilled water and reweighed using a balance with a sensitivity of ±0.1 mg. The average values of the mass loss data were used to calculate parameters such as corrosion rate, inhibition efficiency and recovery rate using the following relationships:

$$W = \frac{\Delta m}{St} \tag{1}$$

$$EI(\%) = \frac{W_0 - W}{W_0} \times 100 \tag{2}$$

$$\theta = \frac{W_0 - W}{W_0} \tag{3}$$

where W_0 and W are the corrosion rate in the absence and presence of the inhibitor respectively, Δm is the mass loss, S is the total surface area of the copper sample and t is the immersion time.

3. Results and Discussion

3.1. Effects of concentration and temperature

Figures 2 and 3 show the evolution of corrosion rate and inhibition efficiency as a function of temperature and piroxicam concentration, respectively.

Figure 3 shows that the inhibitory efficacy of piroxicam increases with both temperature and inhibitor concentration. There is therefore the formation of a barrier consisting of the Cu-piroxicam complex which isolates the metal from its environment.

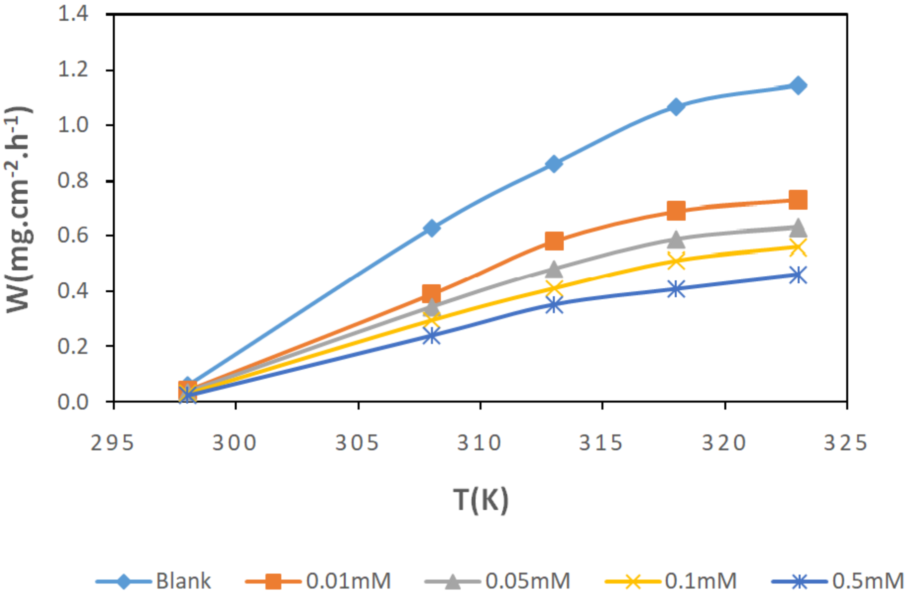

Figure 2. Corrosion rate versus temperature curve for different concentrations of piroxicam.

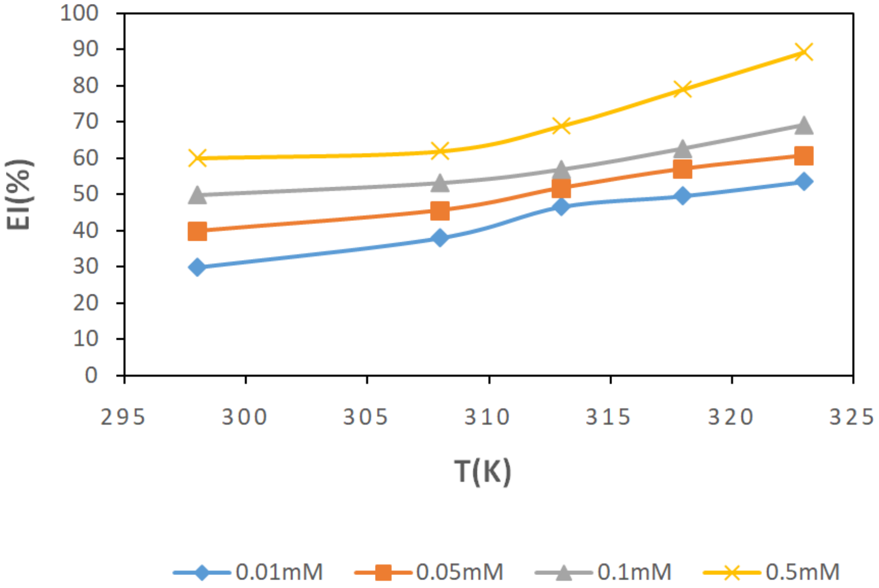

Figure 3. Inhibition efficiency versus temperature for different concentrations of piroxicam.

3.2. Adsorption isotherms

The model that best fits the adsorption process was chosen using the values of the determination coefficient R^2 of the graphs: the highest value of the determination coefficient corresponds to the best model. The isotherm models in their respective modes are described by the following equation:

$$f(\theta, x)\exp(-2a\theta) = K_{ads}C_{inh} \tag{4}$$

where $f(\theta, x)$ represents the configuration factor and depends on the physical model and the assumptions underlying the derivation of the model, θ is the metal surface coverage rate, C_{inh} is the inhibitor concentration, a is a molecular interaction parameter, x is the number of water molecules replaced by an organic molecule, K_{ads} is the equilibrium constant of the adsorption process. The equations of the attempted models are listed in Table 1.

Table 1. Equations of the studied isotherms.

Isotherm	Equations
Langmuir	$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$
Temkin	$\theta = \frac{2{,}303}{f}[logK_{ads} + logC_{inh}]$
El-Awady	$log\left(\frac{\theta}{1-\theta}\right) = logK + y\ logC_{inh}$
Freundlich	$log(\theta) = logK_{ads} + n\ logC_{inh}$

C_{inh} is the concentration of piroxicam;

K_{ads} is the equilibrium constant of the adsorption process,

f is an energy inhomogeneity factor of the surface;

θ is the surface coverage;

K_{ads}=$K'^{1/y}$

$1/y$ is the number of active sites occupied by an inhibitor molecule.

Figures 4, 5, 6 and 7 give graphs of the isotherms studied.

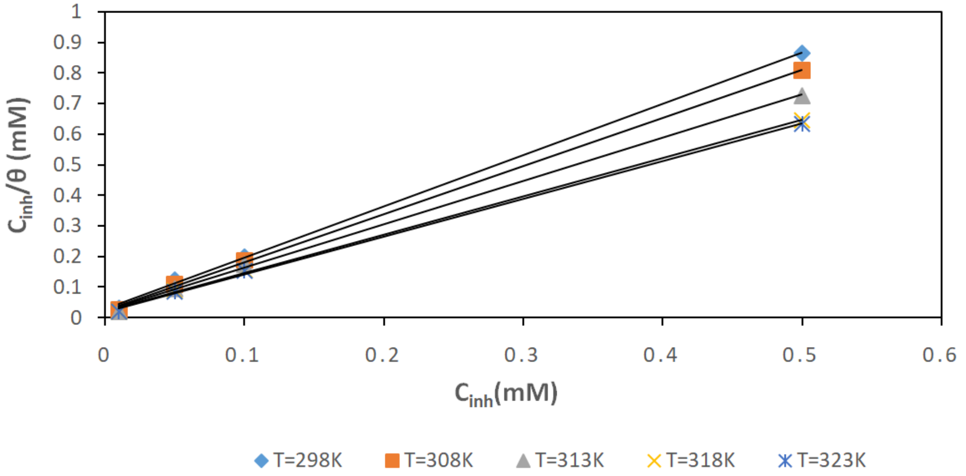

Figure 4. Langmuir isotherms for the adsorption of piroxicam on copper in 1M HNO_3 medium at different temperatures.

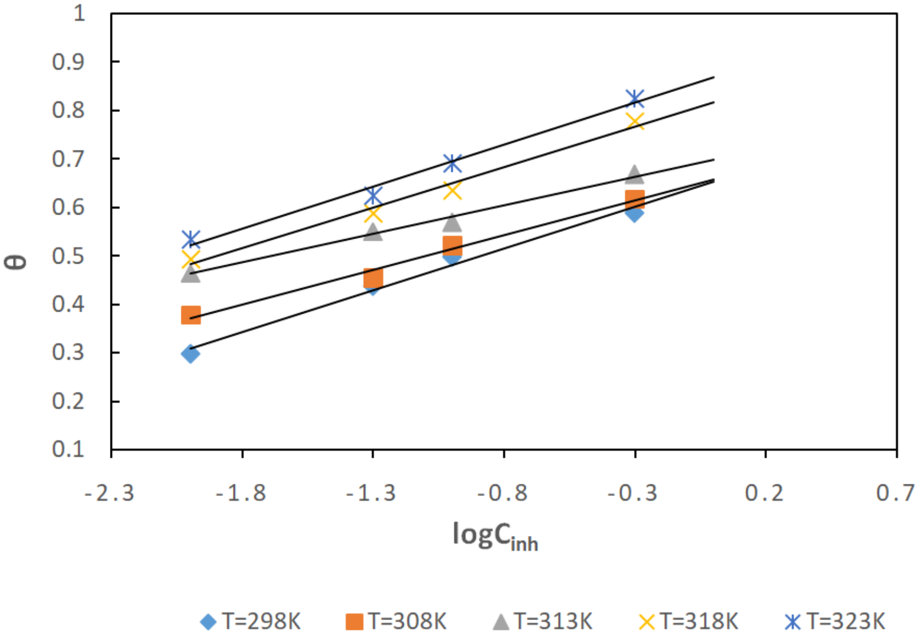

Figure 5. Temkin isotherms for the adsorption of piroxicam on copper in 1M HNO_3 medium at different temperatures.

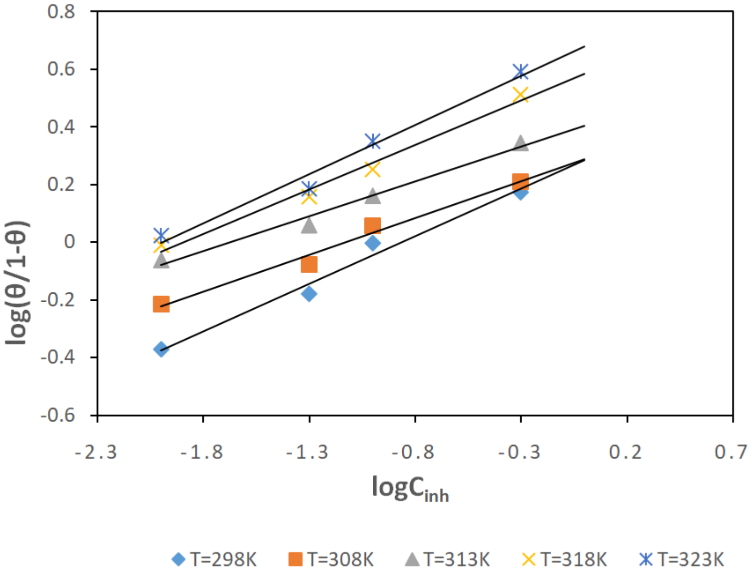

Figure 6. El-Awady isotherms for the adsorption of piroxicam on copper in 1M HNO_3 medium at different temperatures.

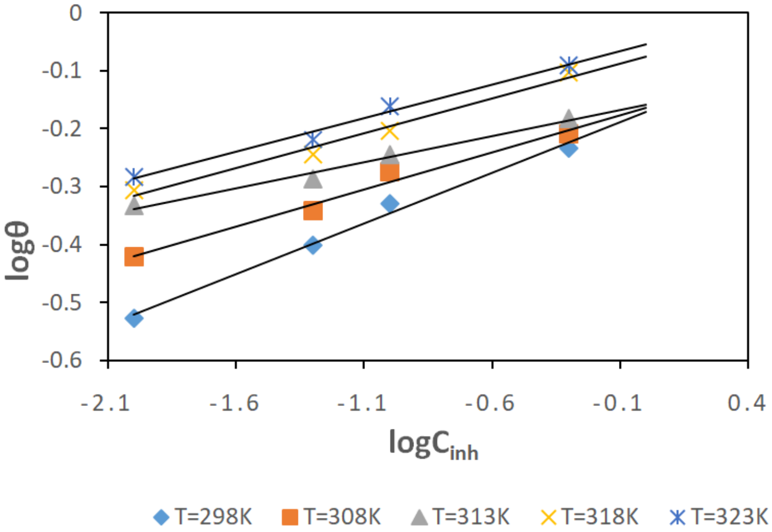

Figure 7. Freundlich isotherms for the adsorption of piroxicam on copper in 1M HNO_3 medium at different temperatures.

All the isotherms studied give straight lines as shown in Figures 4, 5, 6 and 7.

Table 2 gives the different parameters of the studied isotherms.

Table 2. Isotherms parameters for various temperatures.

Isotherm	$T(K)$	R^2	Slope	Intercept
Langmuir	298	0.9992	1.6072	0.0302
	308	0.9993	1.5754	0.0234
	313	0.9987	1.4158	0.0216
	318	0.9989	1.2546	0.0201
	323	0.9988	1.2327	0.02
Temkin	298	0.9852	0.1721	0.6538
	308	0.9878	0.143	0.6581
	313	0.9905	0.1176	0.6986
	318	0.9863	0.167	0.8172
	323	0.9881	0.1727	0.8681
El-Awady	298	0.981	0.3294	0.2838
	308	0.9827	0.2548	0.2863
	313	0.9842	0.2408	0.4027
	318	0.9854	0.3079	0.5837
	323	0.9804	0.3405	0.9627
Freundlich	298	0.9909	0.1746	-0.1709
	308	0.9806	0.1278	-0.1644
	313	0.9854	0.0898	-0.1582
	318	0.9819	0.1199	-0.0761
	323	0.9864	0.1158	-0.054

By looking Table 2, it is clear that the correlation coefficients of Langmuir isotherm are closer to unity than the other isotherms. Thus, this isotherm better reflects piroxicam behavior with respect to copper corrosion in 1M HNO_3.

Nevertheless, Temkin and El-Awady models can be applied. For Temkin model [14], the parameter f (where $2.303/f$ is the slope of straight lines) having a positive value, there would be repulsion forces between the molecules adsorbed on copper. As for El-Awady model [15], the inverse of the slopes $(1/y)$ of the straight lines obtained is greater than unity, this means that a piroxicam molecule occupies more than one site. Langmuir adsorption model requires that the interactions between adsorbed particles are negligible and that each site can adsorb only one particle [16]. In this case, piroxicam adsorption on copper is not rigorously done according to Langmuir model; it is done according to the modified Langmuir isotherm or Villamil model [17]. This model represented by the equation:

$$\frac{C_{inh}}{\theta} = \frac{n}{K} + nC_{inh} \tag{5}$$

$n\theta$ is the effective recovery rate.

3.3. Determination of thermodynamic quantities related to the adsorption of piroxicam on copper

The knowledge of the suitable adsorption isotherm allows to determine the thermodynamic adsorption parameters. The change in free energy of adsorption ΔG^0_{ads} is calculated using the following relation [18]:

$$\Delta G^0_{ads} = -RTln(55.5K_{ads}) \tag{6}$$

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

The values of ΔG^0_{ads} obtained are given in Table 3.

Table 3. Values of thermodynamic quantities related to the adsorption of piroxicam on copper.

$T(K)$	K_{ads} (M^{-1})	ΔG^0_{ads} (kJ.mol^{-1})	ΔH^0_{ads} (kJ.mol^{-1})	ΔS^0_{ads} (J.mol^{-1}.K^{-1})
298	33113	-35.74	13.44	165.4
308	42735	-37.59		
313	46296	-38.41		
318	49751	-39.21		
323	50000	-39.84		

The values of ΔG^0_{ads} are negative for all temperatures explored; this means that the adsorption of piroxicam on copper is spontaneous. According to the literature [19], a value of ΔG^0_{ads} lower than -40 kJ.mol^{-1} would indicate a chemical adsorption process (chemisorption) whereas a value higher than -20 kJ.mol^{-1} would indicate a physical adsorption process (physisorption). For values between -40 kJ.mol^{-1} and -20 kJ.mol^{-1}, both types of adsorption would exist. With regard to the values contained in the table, we can deduce that the adsorption of piroxicam on copper is chemisorption.

The variations in enthalpies ΔH^0_{ads} and entropy ΔS^0_{ads} of adsorption are deduced using the following equation:

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads} \tag{7}$$

where ΔH^0_{ads} and ΔS^0_{ads} are respectively the y-intercept and the opposite of the slope of the straight line obtained from the curve of ΔG^0_{ads} versus temperature (Figure 8).

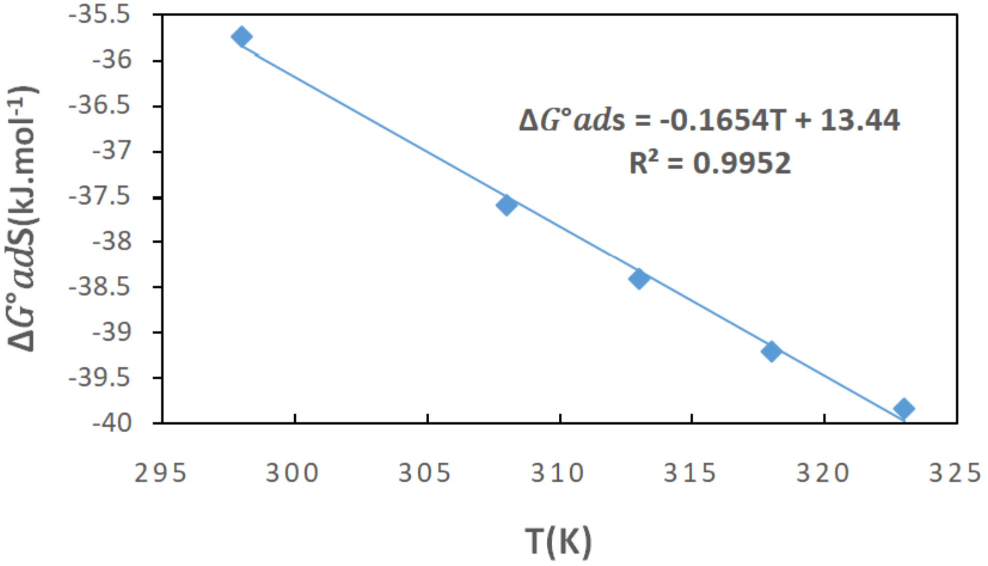

Figure 8. Free enthalpy changes versus temperature.

The negative values of the free adsorption enthalpy show the spontaneous nature of the adsorption phenomenon. Figure 8 shows that the plot of ΔG^0_{ads} as a function of temperature is a straight line with a slope (ΔS^0_{ads}) and an intercept (ΔH^0_{ads}). According to the equation of this line, we see that ΔH^0_{ads} = 13.44 kJ.mol^{-1} and ΔS^0_{ads} = 165.4 J.mol^{-1} K^{-1}. The positive sign of the variation of adsorption enthalpy indicates an endothermic adsorption process while the positive sign of the variation of entropy shows that the disorder increases in the adsorption phase probably due [20] to desorption water molecules.

To interpret the mode of adsorption of piroxicam, we used the Adejo-Ekwenchi and Dubinin-Radushkevich isotherms of respective equations:

$$\log[1/1-\theta] = logK_{AE} + blogC \tag{8}$$

where K_{AE} and b are the isotherm parameters and C the adsorbate concentration.

$$ln\theta = ln\theta_{max} - a\delta^2 \tag{9}$$

with: $$\delta = RTln\left(1 + \frac{1}{MC_{inh}}\right) \tag{10}$$

$E_{ads}^{m} = \frac{1}{\sqrt{2a}}$ (Mean adsorption energy in kJ/mol).

Figures 9 and 10 respectively give the curves of $log(1/1-\theta)$ as a function of $log\ C$ and lnθ as a function of the total charge on the active centers δ^2 . The values of all associated parameters are listed in Tables 4 and 5 respectively.

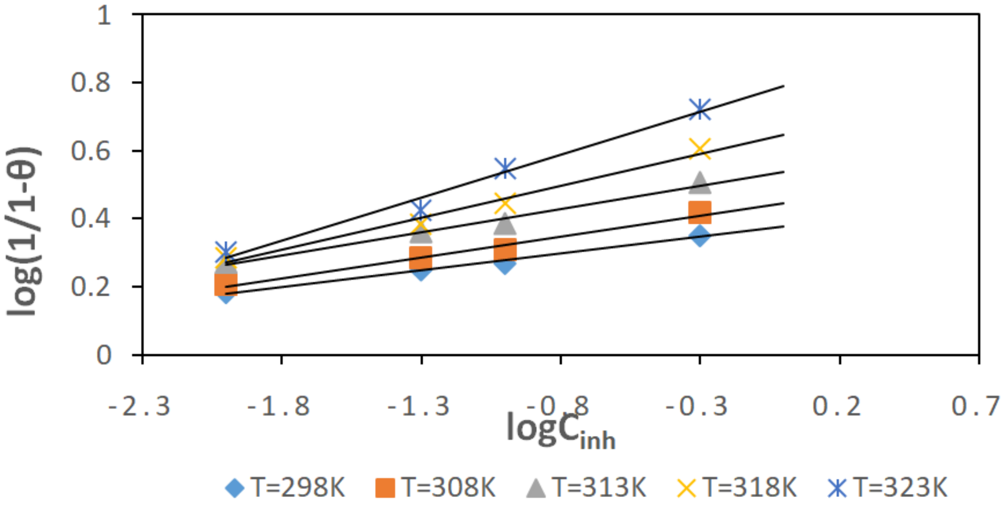

Figure 9. Adejo-Ekwenchi isotherm plots of piroxicam on copper in 1M HNO_3.

The parameters for this isotherm are listed in Table 4

Table 4. Adejo-Ekwenchi isotherm parameters.

$T(K)$	Equations	K_{AE}	b	R^2
298	$log(1/1-\theta) = 0.0978logC_{inh} + 0.3764$	2.379	0.0978	0.9924
308	$log(1/1-\theta) = 0.1221logC_{inh} + 0.4459$	2.792	0.1221	0.9861
313	$log(1/1-\theta) = 0.136logC_{inh} + 0.5376$	3.448	0.136	0.9866
318	$log(1/1-\theta) = 0.1885logC_{inh} + 0.6485$	4.451	0.1885	0.9842
323	$log(1/1-\theta) = 0.2519logC_{inh} + 0.7887$	6.147	0.2519	0.981

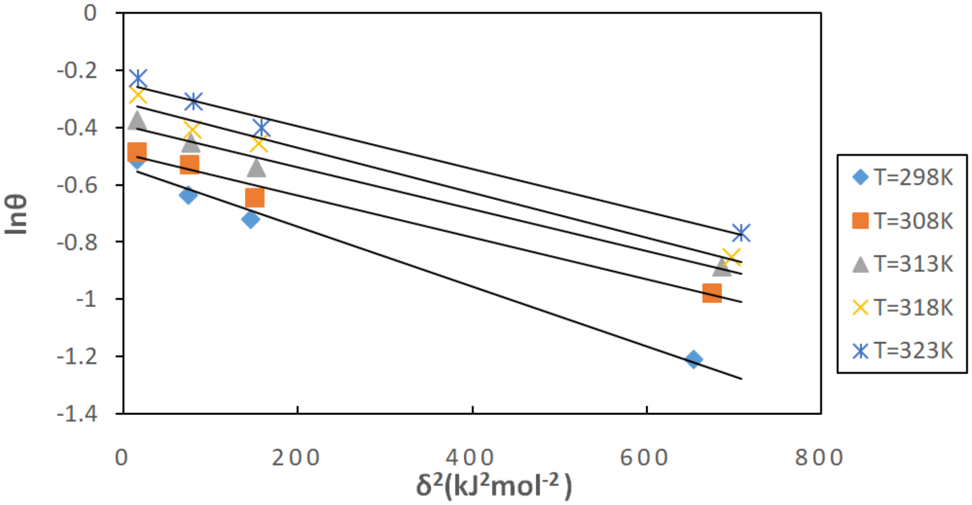

Figure 10. Dubinin-Radushkevich isotherm plots of piroxicam on copper in 1M HNO_3.

Table 5. Dubinin-Radushkevich isotherm parameters.

$T(K)$	Equations	R^2	E_{ads}^{m} (kJ.mol^{-1})
298	$ln\theta = -0.0012\delta^2 - 0.5395$	0.9887	22.36
308	$ln\theta = -0.0007\delta^2 - 0.4937$	0.9825	26.73
313	$ln\theta = -0.0007\delta^2 - 0.3938$	0.9852	26.73
318	$ln\theta = -0.0008\delta^2 - 0.3162$	0.9834	25
323	$ln\theta = -0.0007\delta^2 - 0.2473$	0.9862	26.73

As reflected in Table 4, parameters b and K_{AE} increase with temperature, showing that the adsorption of piroxicam on copper is dominated by chemisorption [21].

It can also be seen that the adsorption energy values E_{ads}^{m} calculated in Table 5 at different temperatures for our inhibitor are greater than 8 kJ/mol. This confirms that piroxicam is chemically adsorbed on copper for all the temperatures considered. It thus defines a single type of adsorption [22].

3.4. Corrosion process activation parameters

The thermodynamic activation quantities (activation energy E_a, activation enthalpy change ΔH_a^* and activation entropy change ΔS_a^*) for the corrosion process were determined from the Arrhenius and transition state equations [23]:

$$logW = logA - \frac{E_a}{2{,}303RT} \tag{11}$$

$$log\left(\frac{W}{T}\right) = \left[log\left(\frac{R}{\aleph h}\right) + \frac{\Delta S_a^*}{2{,}303R}\right] - \frac{\Delta H_a^*}{2{,}303RT} \tag{12}$$

W is the corrosion rate, R is the perfect gas constant, A is the pre-exponential factor, h is Planck's constant and $\aleph$ is Avogadro's constant, E_a activation energy, ΔH_a^* change in activation enthalpy and ΔS_a^* change in activation entropy. Figure 10 shows the Arrhenius curves $logW$ versus $1/T$ for copper in 1M HNO_3 nitric acid solution without and with different concentrations of piroxicam. Straight lines are obtained with correlation coefficients ($R^2 >$ 0.9). The slopes ($-\frac{E_a}{2{,}303R}$) of these straight lines are used to calculate the apparent activation energy (E_a). The values of the thermodynamic activation quantities are given in Table 5.

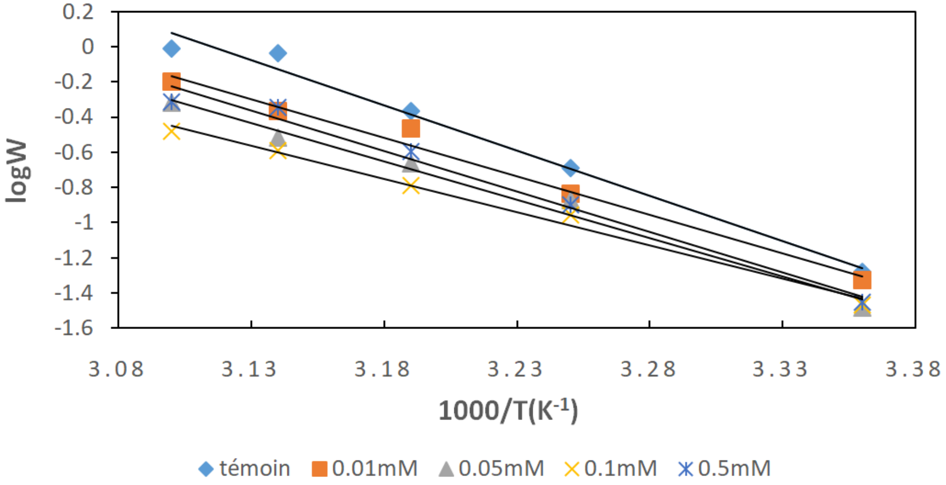

Figure 10. $logW$ versus $1/T$ for the corrosion of copper in 1M HNO_3 with and without piroxicam.

Table 6. Thermodynamic values of copper dissolution in 1M HNO_3 without and with different concentrations of piroxicam.

Concentration	$E_a(kJ.mol^{-1})$	$\Delta H_a^*(kJ.mol^{-1})$	$\Delta S_a^*(J.mol^{-1}.K^{-1})$
0	98.628	54.290	-78.310
0.01	83.822	71.861	-20.021
0.05	83.487	68.551	-40.420
0.1	72.483	64.883	-55.939
0.5	87.805	65.280	-55.140

The activation energy in the absence of piroxicam is higher than the activation energies in its presence; this would indicate according to the literature [24] that chemisorption is prevalent.

Figure 11 illustrates the $log(W/T)$ versus $1/T$.

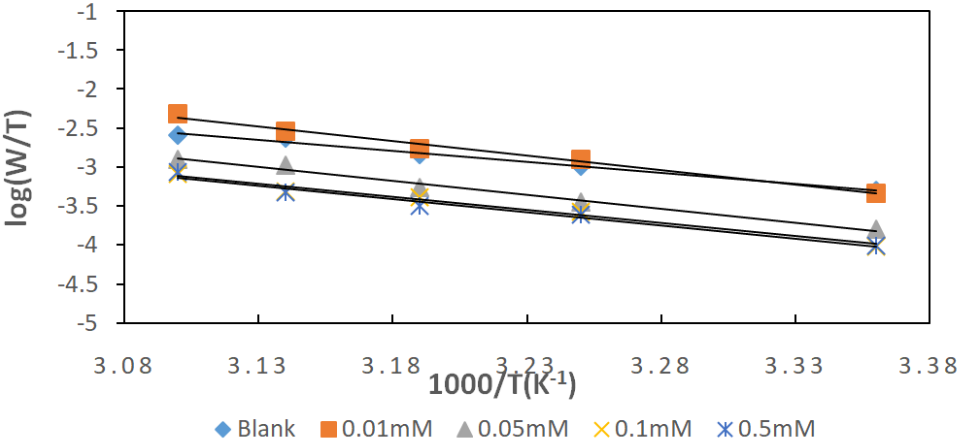

Figure 11. $log(W/T)$ versus $1/T$ for copper corrosion in 1M HNO_3 with and without piroxicam.

The change in activation enthalpy ΔH_a^* is positive, indicating the endothermic nature of the copper dissolution. The activation entropy variation ΔS_a^* is negative, which would reflect [25] some organization during the formation of the activated complex.

4. Conclusion

In the present work the results obtained show that:

- Piroxicam acts as a good copper corrosion inhibitor in a 1M nitric acid medium. Its inhibitory efficiency IE (%) depends on concentration and temperature.

- Piroxicam is adsorbed on copper according to the modified Langmuir isotherm. The calculated thermodynamic quantities related to adsorption and activation show that the mode of adsorption is chemisorption.

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