Research Article

Study of the Inhibitory Performance of Bisoprolol against Copper Corrosion in Nitric Acid

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Abstract

The inhibitory properties of the bisoprolol molecule in the corrosion of copper (Cu) in 1M nitric acid were studied using the mass loss technique and the theoretical method based on density functional theory (DFT). The results show that the inhibition efficiency of bisoprolol increases with concentration and temperature. The study of adsorption isotherms showed that bisoprolol adsorbs on copper according to the Villamil isotherm. The Dubinin Radushkevich and Adejo-Ekwenchi isotherms showed that the adsorption of the molecule on copper is essentially chemisorption. The thermodynamic functions of adsorption and activation were determined and analysed. The adsorption of the bisoprolol molecule on the copper surface is an endothermic and spontaneous process. DFT calculations based on the B3LYP functional and the 6-311G (d,p) basis set led to the determination of global parameters. The study showed conformity between experimental and theoretical results.

Keywords: Copper, nitric acid, corrosion inhibition, bisoprolol, mass loss technique, DFT

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Introduction

Copper and its alloys [1, 2] are widely used in many industrial equipments, they have excellent thermal conductivity, good corrosion resistance and mechanical workability and are widely used in heating and cooling systems. Copper has recognized bactericidal properties, it has properties for purifying pipes and very important physical properties. Corrosion of copper and its alloys by corrosive media, such as nitric acid solutions, is inevitable and limits its application in industry.

Of the various methods available to mitigate the corrosion of copper and its alloys, the use of inhibitors is one of the most practical and cost-effective choices. Therefore, organic compounds, which contain either heteroatoms, free doublets of nitrogen, oxygen, sulphur atoms andπ-leaves, generally exhibit good inhibitory properties [3-5]. The inhibitory action of these organic compounds is attributed to their interactions with the copper surface via their adsorption. The polar functional groups [6] are considered to be the reaction centers that stabilize the adsorption process. In general, the adsorption of an inhibitor on a metal surface [7] depends on the nature of the surface, the mode of adsorption, the molecular structure and the type of electrolyte solution.

Many molecules and drugs are enzyme inhibitors, so that the discovery of these molecules and the improvement of their inhibitory properties are important research topics in biochemistry and pharmacology [8].

This work, which is a contribution to the study of the inhibition of metal corrosion in an acidic environment, aims to study the behaviour of bisoprolol with respect to copper corrosion in 1M nitric acid.

Materials and methods

Copper specimens

The copper samples were in the form of a rod 10 mm long and 2.2 mm in diameter. It is a commercial copper of 95% purity.

The molecule studied

Bisoprolol is a molecule of the beta-blocker class, used to treat high blood pressure, angina pectoris or myocardial infarction or very often for the treatment of heart failure. It is also known as 1-(propan-2-ylamino)-3-[4-(2-propan-2-yloxyethoxymethyl) phenoxy] propan-2-ol with a molar mass M= 325.443 g/mol. **Figure 1** shows the molecular structure of bisoprolol.

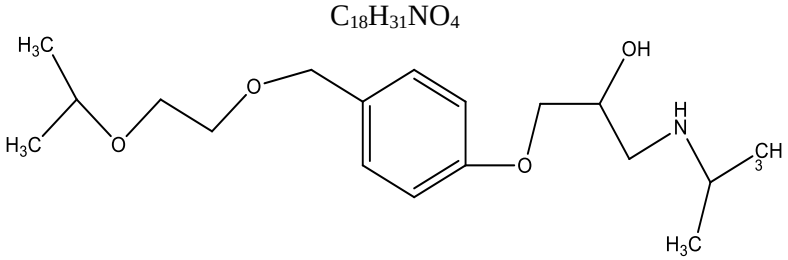

Figure 1 : molecular structure of bisoprolol

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 double distilled water. The blank was a 1 M HNO3 solution. The bisoprolol solutions prepared ranged from 0.01 to 0.5mM.

Mass loss method

The mass loss method [9-11] is one of the most widely used methods for assessing corrosion inhibition of metals due to its simplicity and reliability of measurement. Mass loss measurements were carried out by total immersion of the pre-weighed copper sample in 100 ml capacity beakers containing 50 ml of the test solution maintained at a temperature of (298K to 323K). The samples were recovered one hour later and rinsed thoroughly with distilled water, cleaned, dried in acetone and reweighed using a balance with a sensitivity of ±0.1 mg. All tests were performed in triplicate to ensure reliability of the results. Weight loss was considered as the difference between the initial weight and the weight after 1 h of immersion. The average values of the mass loss data were used to calculate parameters such as corrosion rate, inhibition efficiency and surface coverage using the following relationships:

$$W = \frac{\Delta m}{St} \quad (1)$$

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

$$\theta = \frac{W_0 - W}{W_0} \quad (3)$$

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.

Quantum chemistry calculations

In order to explain the most important electronic effects exhibited by bisoprolol in the inhibition of copper corrosion, quantum chemical parameters were calculated. All calculations were performed in the gas phase using the Gaussian 09 software [12]. By improving the calculation method, density functional theory (DFT) was widely used due to its accuracy and low computational cost to calculate a wide variety of molecular properties and provided reliable results that are consistent with the experimental data [13]. The molecular configuration of the inhibitor was geometrically optimised by this theory (DFT) with the B3LYP function [14] (Becke's three-parameter hybrid correlation function with Lee-Yang-Parr) on a 6-311 G (d,p) basis set which led to a total energy of the molecule under study (bisoprolol) with good accuracy and acceptable CPU time.

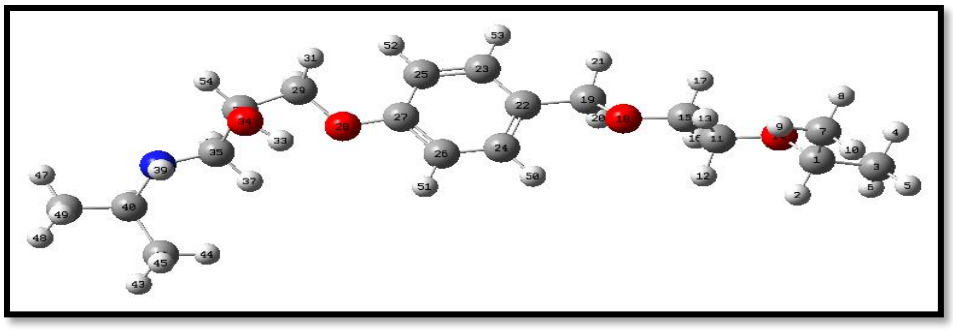

Figure 2 Molecular structure of bisoprolol obtained from B3LYP/6-311G (d,p)

Results and Discussion

Figures 3 and **4** show the evolution of corrosion rate and inhibition efficiency as a function of temperature and bisoprolol concentration, respectively.

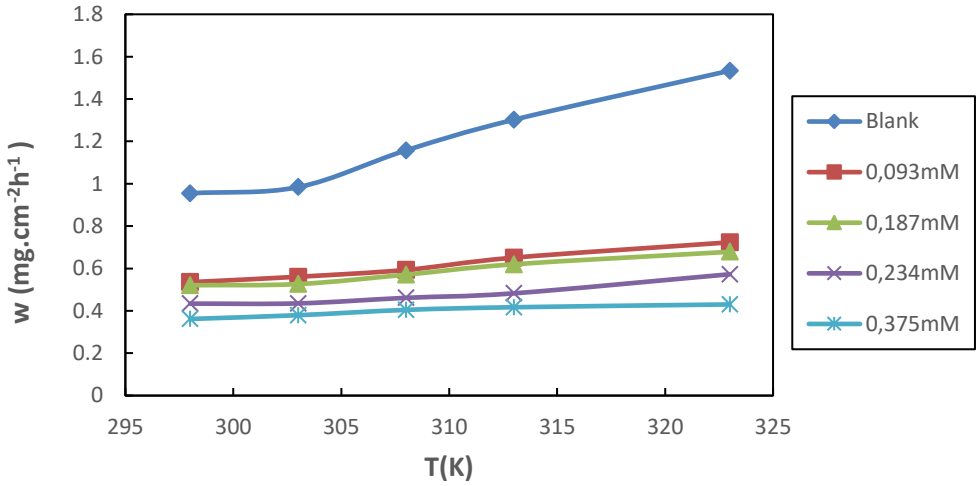

Figure 3 Corrosion rate versus temperature curve for different concentrations of bisoprolol

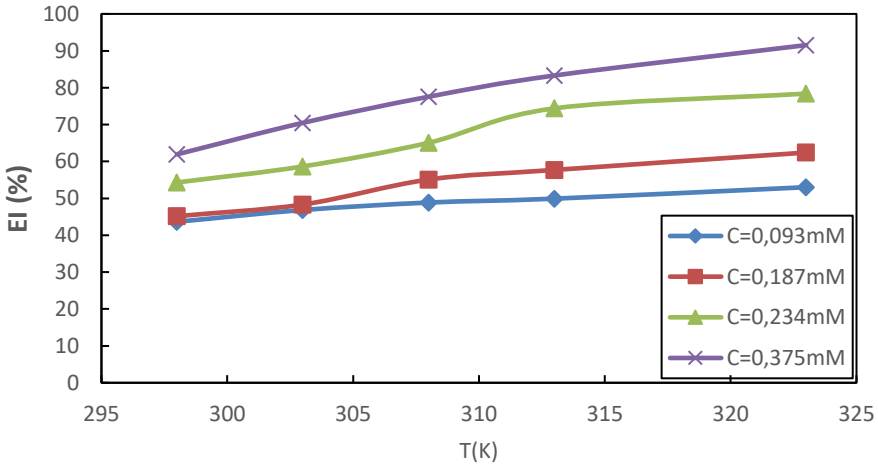

Figure 4 Inhibition efficiency as a function of temperature for different concentrations of bisoprolol

Figure 3 shows that the inhibitory efficiency of bisoprolol increases with both temperature and inhibitor concentration. This could be explained by a higher copper surface coverage when the inhibitor concentration increases and especially by the formation of a Cu-bisoprolol complex film (the vacant d-orbitals of the Cu^{2+} ions receive electrons from the bisoprolol molecules. The increase in temperature increases the number of Cu^{2+} ions on the surface, which favours a greater overlap (formation of a barrier consisting of the Cu-bisoprolol complex) that isolates the metal from its environment. This leads to an increase in inhibitory efficiency as the temperature increases.

Adsorption isotherms

The adsorption isotherms study involved in the process of metals corrosion inhibition by organic molecules allows to show how these compounds bind to the surface of a metal. Indeed The adsorption of an organic adsorbate onto metal–solution interface can be represented by a substitutional adsorption process between the organic molecules in the aqueous solution phase (Org (sol)) and the water molecules on the metallic surface (H_2O(ads)) according to the equation [15]:

$$(sol) + xH2(ads) \rightleftarrows Org(ads) + xH2O\ sol \qquad (4)$$

Where Org(sol) and Org(ads) are respectively the organic species dissolved in the aqueous solution and adsorbed onto the metallic surface. H_2O(sol) and H_2O(ads) are respectively the water molecule in the bulk solution and that adsorbed onto the metallic surface; *x* is the size ratio representing the number of water molecules replaced by one organic adsorbate. The equations of the attempted models are listed in **Table 1**. **Figures 5-7** show the representation of these different isotherms.

Table 1 Equations of the studied isotherms

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

C_{inh} is bisoprolol's concentration; K_{ads} is the equilibrium constant of the adsorption process, *f* is a factor of energetic inhomogeneity in the surface; θ is surface coverage; $K_{ads}=K'^{1/y}$; 1/*y* is active sites occupied by an inhibitor molecule.

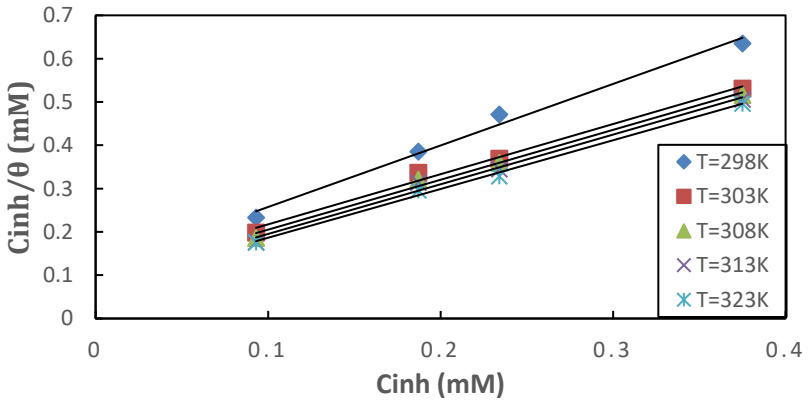

Figure 5 Langmuir adsorption isotherm plots of bisoprolol on copper in 1M HNO_3

Table 2 gives the different parameters of the studied isotherms. By looking the 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 bisoprolol behavior with respect to copper corrosion in 1M HNO_3.

However there is a divergence of the unit slope [16] due to interactions between adsorbed species on the copper surface as well as changes in Gibbs energy values with increasing coverage of the surface. Therefore, a modified Langmuir's equation, suggested elsewhere [17] and presented in the equation below, which accounts for this discrepancy, can be used:

$$\frac{C_{inh}}{\theta} = \frac{n}{K} + nC_{inh} \qquad (5)$$

$n\theta$ is the effective recovery rate.

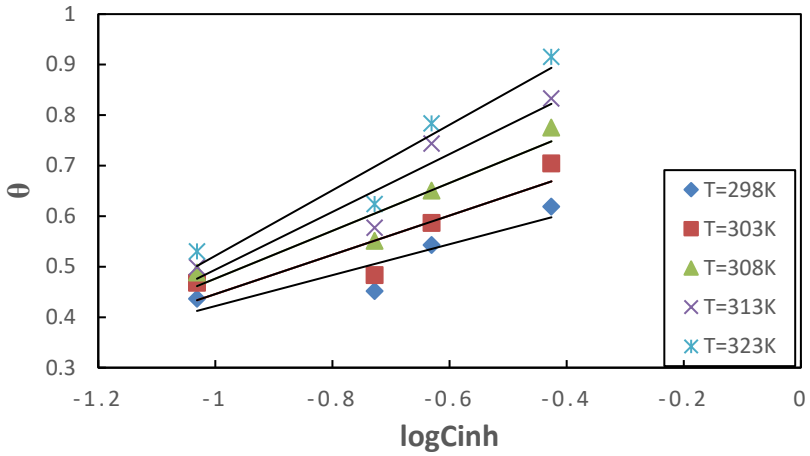

Figure 6 Temkin adsorption isotherm plots of bisoprolol on copper in 1M HNO_3

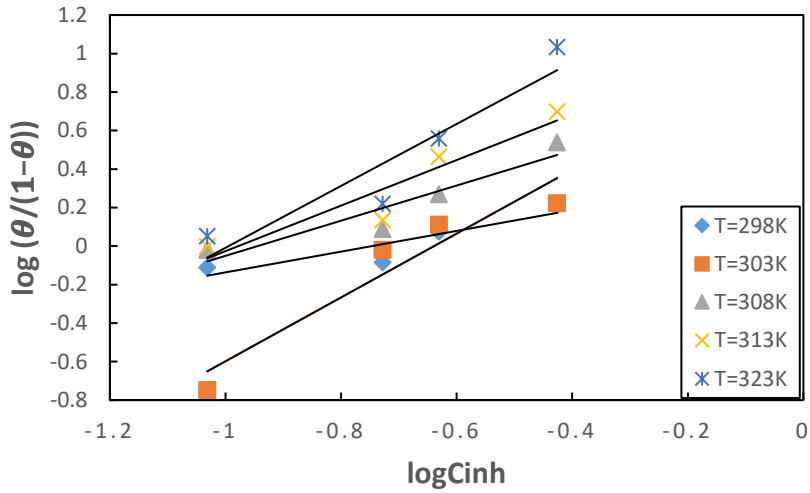

Figure 7 EL-awady adsorption isotherm plots of bisoprolol on copper in 1M HNO_3

Table 2 Isotherms parameters for various temperatures

Isotherm	T(K)	R^2	Slope	Intercept
Langmuir	298	0.989	1,4207	0,1154
	303	0.991	1,1582	0,1016
	308	0.993	1,152	0,09
	313	0.991	1,1471	0,0805
	323	0.996	1,1253	0,074
Temkin	298	0.818	0,306	0,7281
	303	0.801	0,3885	0,8343
	308	0.906	0,4734	0,9498
	313	0.894	0,572	1,066
	323	0.917	0,6483	1,1699
El-Awady	298	0.818	0,5387	0,4021
	303	0.909	1,6577	1,0593
	308	0.889	0,9129	0,8622
	313	0.886	1,183	1,1566
	323	0.874	1,6074	1,5985

Thermodynamic adsorption functions

The knowledge of the suitable adsorption isotherm allows to determine the thermodynamic adsorption parameters. The change in adsorption enthalpy ΔG^0_{ads} was calculated using the following equation:

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

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

Figure 8 presents the plot of ΔG^0_{ads} versus temperature. The plot is a straight line with a slope (-ΔS^0_{ads}) and an intercept (ΔH^0_{ads}).The obtained values are listed in **Table 3**.

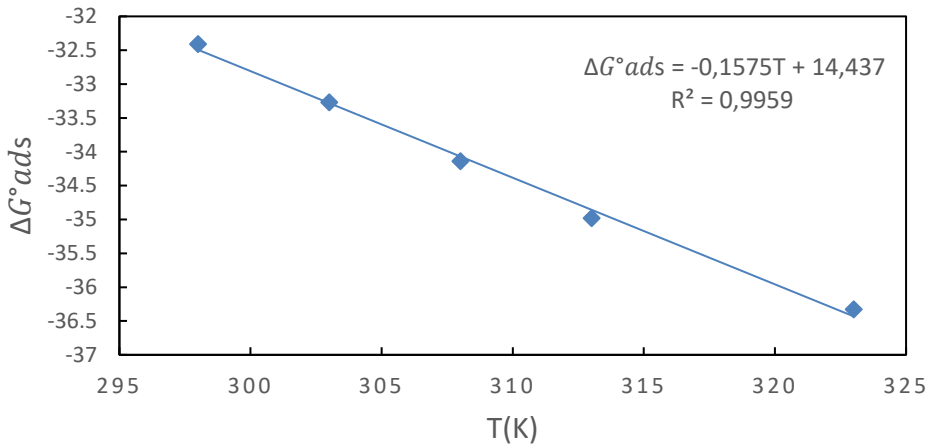

Figure 8 Free enthalpy changes versus temperature

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

T(K)	$K_{ads}(10^3 M^{-1})$	$\Delta G^0_{ads}(kJmol^{-1})$	$\Delta H^0_{ads}(kJmol^{-1})$	$\Delta S^0_{ads}(Jmol^{-1}K^{-1})$
298	8,66	-32,41	14,44	157,5
303	9,84	-33,27		
308	11,11	-34,14		
313	12,42	-34,98		
323	13,51	-36,33		

The values of ΔG^0_{ads} are negative for all temperatures explored; this means that the adsorption of bisoprolol on copper is spontaneous. According to the literature [18], 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 bisoprolol on copper takes place according to the two adsorption modes (physisorption and chemisorption).

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

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

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).

The negative values of the free adsorption enthalpy show the spontaneous character of the adsorption phenomenon. Figure 8 shows that the plot of ΔG^0_{ads} versus temperature is a straight line with a slope ($-\Delta S^0_{ads}$) and an intercept (ΔH^0_{ads}). From the equation of that straight line, it can be seen that ΔH^0_{ads} = 14,44 kJ.mol^{-1} and ΔS^0_{ads}= 157,5 J.mol^{-1} K^{-1}. The positive sign of change in adsorption enthalpy indicates an endothermic adsorption process while the positive sign of change in entropy shows that disorder increases in adsorption phase probably due [19] to the desorption of water molecules.

Adsorption type

Analysing the values of the change in adsorption free enthalpy (ΔG^0_{ads}) ranging from -40 kJ.mol^{-1} to -20 kJ.mol^{-1}, showing that thermodynamic parameters point toward both physisorption and chemisorption. Therefore, there is an ambiguity in using solely both variations in IE (%) with temperature and values of ΔG^0_{ads} as criteria to distinguish between physical and chemical adsorption.

To resolve this ambiguity, we used Adejo-Ekwenchi adsorption and Dubinin Radushkevich isotherms.

Adejo-Ekwenchi adsorption isotherm: The Adejo-Ekwenchi isotherm is based on the following equation:

$$\log[1/(1-\theta)] = logK_{AE} + b\ log\ C_{inh} \quad (8)$$

Where K_{AE} and b are the parameters of the isotherm and C_{inh}, the adsorbate concentration.

The evolution of the parameter b determines [20].the type of adsorption: decrease in values of this parameter indicates physisorption, while increase or fairly constant values signifies chemisorption. **Figure 9** gives the plots of the isotherm.

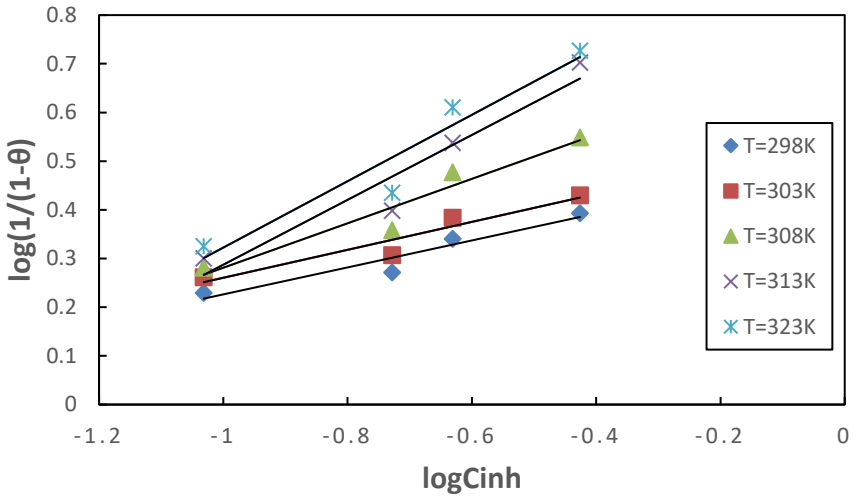

Figure 9 Adejo-Ekwenchi isotherm for bisoprolol on copper surface

All the isotherm parameters are listed in **Table 4**. As reflected in Table 4, parameters b and KAE increase with temperature, showing that the adsorption of bisoprolol on copper is dominated by chemisorption [20].

Table 4 Adejo-Ekwenchi adsorption isotherm parameters

T(K)	b	$logK_{AE}$	K_{AE}	R^2
298	0.2769	0.5033	3.1864	0.921
303	0.2869	0.5474	3.5270	0.916
308	0.4563	0.7374	5.4626	0.925
313	0.6661	0.9535	8.9846	0.921
323	0.6817	1.0042	10.0972	0.923

Dubinin-Radushkevich isotherm: In order to distinguish between physical and chemical adsorption, the Dubinin-Radushkevich isotherm was also used. The mathematical expression of this isotherm is given as follows [21].

$$ln\theta = ln\theta_{max} - a\delta^2 \quad (9)$$

Where θmax is the maximum surface coverage and δ is the Polanyi potential which is given by:

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

In equation (9), R is the universal gas constant, T is the absolute temperature and $Cinh$ is the concentration en $g.L^{-1}$ of the inhibitor. **Figure 10** gives the plots of $ln\theta$ versus δ^2 for different temperatures.

The parameters of the isotherm are collected in **Table 5**.

The constant "a" gives the mean adsorption energy (E), which represents the transfer energy of 1 mole of adsorbate from infinity (bulk) to the surface of the adsorbent (copper). This energy is given by:

$$E = \frac{1}{\sqrt{2a}} \quad (11)$$

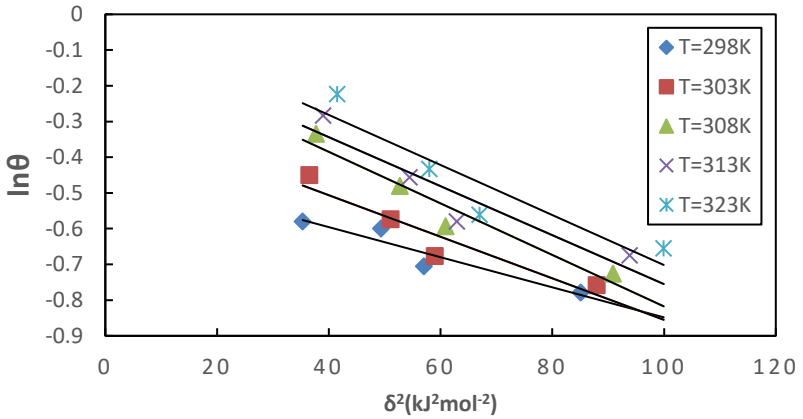

Figure 10 Dubinin Radushkevich isotherm for bisoprolol on copper surface

The magnitude of E gives information about the type of adsorption; if the value of E is less than 8 kJmol^{-1}, physical adsorption [21] is predominant. The values of E collected in Table 3 indicate that chemisorption is predominant. This confirms that Bisoprolol is chemically adsorbed on copper for all the temperatures considered. It thus defines a single type of adsorption [22].

Table 5 Dubinin Radushkevich adsorption isotherm parameters

T(K)	R^2	a (kJ^{-2}mol^2)	E_m (kJ.mol^{-1})	θ_{max}
298	0.896	0.0042	10.51	0.6523
303	0.893	0.0058	9.28	0.7605
308	0.938	0.0072	8.33	0.9082
313	0.875	0.0068	8.57	0.9329
323	0.923	0.007	8.45	0.9988

Activation parameters of the corrosion process

The corrosion rates were evaluated at different temperatures in the absence and presence of Meloxicam; they were used to calculate the activation energy of the metal dissolution. The Arrhenius equation [23] and the transition state equation [24] were:

$$W = Aexp(-\frac{E_a}{RT}) \qquad (12)$$

$$W = \frac{R.T}{\aleph.h} exp\left(\frac{\Delta S_a^*}{R}\right).exp\left(-\frac{\Delta H_a^*}{R.T}\right) \qquad (13)$$

These equations can be taken in the two following forms:

$$\log W = \log K - \frac{E_a}{2{,}3RT} \qquad (14)$$

$$W = \frac{R.T}{\aleph.h} exp\left(\frac{\Delta S_a^*}{R}\right).exp\left(-\frac{\Delta H_a^*}{R.T}\right) \qquad (15)$$

Where R is the universal gas constant, T is the absolute temperature, $\aleph$ is the Avogadro's number and h is the Planck's constant.The plots of logW = f(1/T) and log W/T = g(1/T) (**Figures 10** and **11**) led to the activation parameters (Ea, ΔH_a^*, ΔS_a^*).

Ea and ΔH_a^* were obtained respectively from the slopes of the straight lines associated to (14) and (15), while ΔSa derived from the intercept of the straight line obtained with equation (14).

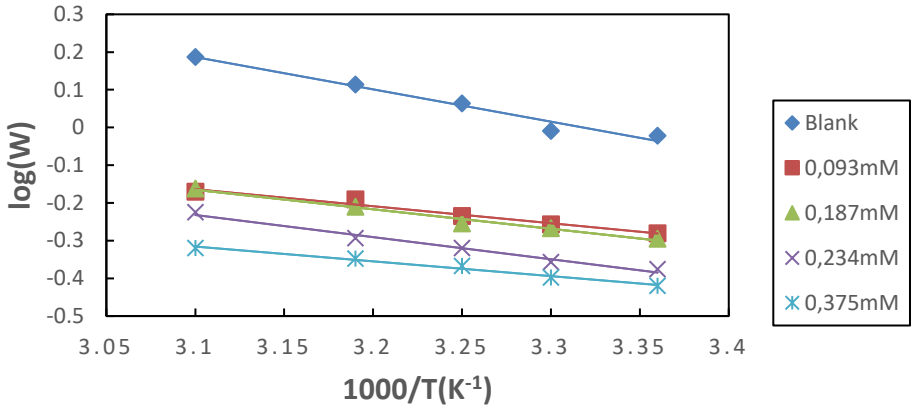

Figure 11 logW versus 1/T for different concentrations.

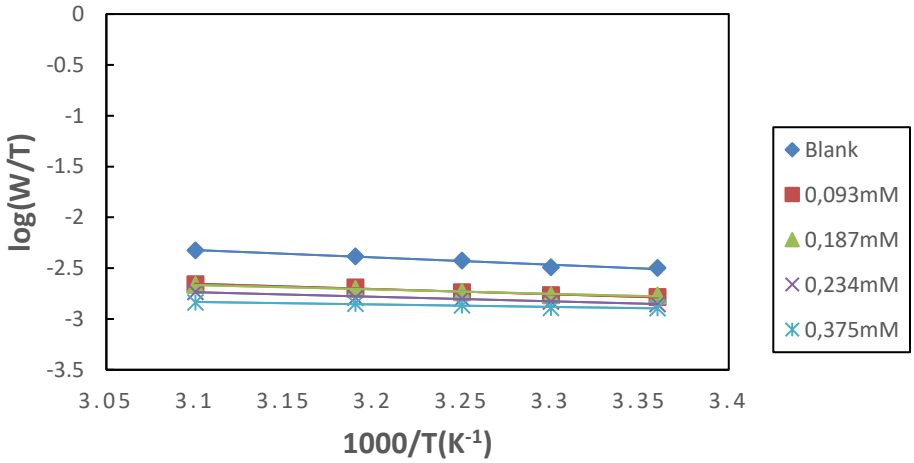

Figure 12 log (W/T) versus 1/T for different concentrations

The parameters of the dissolution of copper in the absence or presence of bisoprolol in the studied environment are listed in **Table 6**.

The activation energy in the absence of bisoprolol (Blank) is higher than the activation energies in its presence; this would indicate according to the literature [25] that chemisorption is prevalent. The obtained values ofΔH_a^* are in good agreement with the calculated values from the equation below:

$$\Delta H_a^* = E_a - \mathrm{RT} \qquad (16)$$

Table 6 Activation parameters of the corrosion of copper in 1M HNO_3 in the absence and presence of bisoprolol

Concentration (mM)	$E_a(kJ.mol^{-1})$	$\Delta H_a^*(kJ.mol^{-1})$	$\Delta S_a^*(J.mol^{-1}.K^{-1})$
0	16,39	13,80	-199,24
0,093	11,71	9,90	-217,86
0,187	9,89	8,17	-223,30
0,234	11,23	8,59	-223,33
0,375	7,5	4,66	-240,01

The positive sign of the variation of activation enthalpy (ΔH_a^*) [26] shows that the dissolution the copper is an endothermic process, whereas the negative sign of the variation of activation entropy (ΔS_a^*) indicates that the activation complex represents an association rather than a dissociation. Studies have shown that bisoprolol has a higher inhibitory efficacy than atenolol in the temperature range studied.

Table 7 Comparison table of the inhibitory efficiencies of two molecules during the corrosion of copper in a 1M HNO3 medium

Temperatures	30(°C)	35 (°C)	40 (°C)	45(°C)	Molécules
EI(%)	59,18(%)	62,9(%)	65,38(%)	70,13(%)	ATENOLOL
EI(%)	70,47(%)	77,55(%)	83,30(%)	91,54(%)	BISOPROLOL

Quantum chemical considerations

According to the frontier molecular orbitals theory [27] K. Fukui, Springer-Verlag, New-York, 1975.], transition of an electron is due to the interaction between frontier orbitals. Molecules with high E_{HOMO} values [27] have the ability to donate electrons to the metal surface atoms with empty molecular orbitals. Conversely, molecules with low E_{LUMO} values [28] A. Domenicano, I. Hargittai, Oxford University Press, New York, 1992.] are able to accept electrons from the metal. The calculated quantum descriptors are reported in **Table 8**.

Table 8 bisoprolol descriptor parameters obtained from B3LYP/6-311G (d,p)

Parameters	Values
E_{LUMO} (eV)	-0.419
E_{HOMO} (eV)	-5.916
ΔE (eV)	5.497
μ (D)	1.9205
I (eV)	5.916
A (eV)	0.419
χ (eV)	3.1675
η (eV)	2.7485
S $(eV)^{-1}$	0.3638
ΔN	1.4821
ω	1.8251

The parameter E_{HOMO} (energy of the highest occupied molecular orbital) corresponds to the area in the molecule where electrons can be given to electrophile systems; thus, the higher, the value, the higher the tendency of the molecule to donate electrons to an appropriate acceptor. In our case the Meloxicam, with E_{HOMO} (-5,916 eV) can be considered [29] as a good electrons donor. On the other hand, E_{LUMO}, the energy of the lowest unoccupied molecular orbital is the energy of the region in the molecule that has the greatest propensity to accept electrons. The value of this parameter in our molecule is (-0,419 eV), indicating [29] a good acceptor capacity. The energy gap HOMO-LUMO is an important parameter that need to be considered. Lower values of this energy [30] lead to higher reactivity tendency, indicating good inhibition efficiency. For the studied molecule, the value of the energy gap (ΔE = 5,497 eV) can be considered [31, 32] as low when comparing to values in the literature.

The dipole moment (μ) result from non-uniformity in the charges distribution in the molecule. Though this parameter is important, there is [33] irregularities in the correlation between it and the inhibition efficiency. In spite of these inconsistent viewpoints the dipole moment remains an important electronic parameter resulting from the non-uniform distribution of charges on various atoms in the molecule.

According to Koopman's theorem [34], E_{HOMO} and E_{LUMO} of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A), respectively by the following relations:

$$I = -E_{HOMO} \quad (17)$$

$$A = -E_{LUMO} \quad (18)$$

The absolute electronegativity (χ) and the global hardness (η) of the inhibitor molecule are approximated as follows [35]:

$$\chi = \frac{I+A}{2} \quad (19)$$

$$\eta = \frac{I-A}{2} \quad (20)$$

Chemical hardness measures the resistance towards the deformation or polarization of the electron cloud of atoms, ions or molecule under small perturbation of chemical reaction. A hard molecule [36] has a large energy gap and a soft molecule has a small energy gap. As hardness, softness (s) is a global chemical descriptor which measures the molecular stability and reactivity; it is given by:

$$S = \frac{1}{\eta} = \frac{2}{I-A} \qquad (21)$$

The obtained values (η = 2,7485 eV and s = 0,3638 $(eV)^{-1}$) show that bisoprolol is a soft molecule when compared to some other molecules in the literature [37]. The global electrophilicity index ω, introduced by Parr as a measure of energy lowering [38] due to maximal electron flow between donor and acceptor is given by:

$$\omega = \frac{\mu_p^2}{2\eta} \qquad (22)$$

Where μ_P is the chemical potential, defined as the first derivative of the total energy with respect to the number of electrons, and therefore as the negative of the electronegativity:

$$\mu_P = \left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\chi \qquad (23)$$

In equation (23), E is the total energy, N is the number of electrons and (r) is the external potential of the system.

The electrophilicity index measures the propensity of chemical species to accept electrons. A high value of ω describes a good electrophile while a small value describes a good nucleophile. In our case, the electrophilicity index of the molecule (ω=1,8251) is high, expressing that bisoprolol is a good electrophile. This reactivity index measures the stabilization in energy when the system acquired an additional electronic charge ΔN from the environment.
Thus the fraction ΔN of electrons transferred from the inhibitor to the metallic surface [38] is given by:

$$\Delta N = \frac{\chi_{Cu}-\chi_{inh}}{2(\eta_{Cu}+\eta_{inh})} \qquad (24)$$

Where χCu, ηCu, χinh and $\eta in\ h$are respectively the absolute electronegativity and hardness of copper and the inhibitor. We use the theoretical value of χCu = 4.98 eV/ and ηCu = 0 [38] for the calculation of the number of electrons transferred.

The fraction of electrons transferred (ΔN) of a molecule reflects its ability to give electrons. According to Lukovits' study, if ΔN < 3.6 then the efficiency of inhibition increases with the molecule's ability to give electrons to the metal [39]. In our work ΔN (1,4821) < 3.6, which shows that bisoprolol has a good inhibition performance in electron donation.

Local Reactivity

Further studies on the spatial distribution of electron density of inhibitor lead to local concentration and local depletion of electron charge density, which allow determining [40, 41] whether the inhibitor undergo electrophilicity or nucleophilicity. To examine the local reactivity behaviour, the condensed Fukui indices were used. The Fukui function is defined as:

$$\boldsymbol{f(\vec{r}) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(\vec{r})}} \qquad (25)$$

Where (r) is the electron density, N is the number of electrons and $v(r)$ is the external potential, acting on an electron (due for instance to atomic nuclei).

The Fukui functions can be written by taking the finite difference approximations as [42]:

$$\boldsymbol{f_k^+ = [q_k(N+1) - q_k(N)]} \quad \text{(for nucleophilic attack)} \qquad (26)$$
$$\boldsymbol{f_k^- = [q_k(N) - q_k(N-1)]} \quad \textbf{(}\text{for electrophilic attack)} \qquad (27)$$

Where qk $(N + 1)$, qk (N), qk $(N - 1)$ are defined as Mulliken charge of the anionic, neutral and cationic species respectively.

Recently, another descriptor known as dual descriptor [43]: and defined as the difference between the nucleophilic and electrophilic Fukui functions has been used

$$\Delta(r) = f_k^+(r) - f_k^-(r) \qquad (28)$$

If $\Delta(r) > 0$, then the site is favoured for a nucleophilic attack, whereas if $\Delta fk\ (r) < 0$, then the site may be favoured for an electrophilic attack. **Figure 13** gives the HOMO and LUMO orbitals of bisoprolol while. Table 8 presents Fukui and dual functions

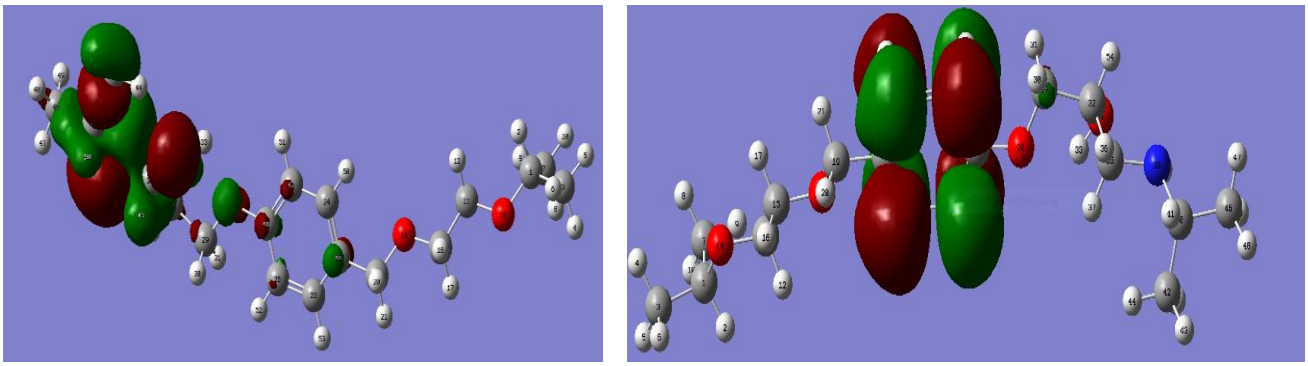

Figure 13 HOMO (left) and LUMO (right) orbitals of bisoprolol by B3LYP/6-311G (d,p)

Table 9 Fukui and dual functions of atoms in bisoprolol, obtained using Mulliken charges

Atoms	q(N)	q(N-1)	q(N+1)	Q(N)	Q(N+1)	Q(N-1)	f_k+	f_k-	Δf_k
C1	0,16034	0,13533	0,14383	5,83966	5,85617	5,86467	0,01651	-0,02501	0,04152
C3	-0,58133	-0,5858	-0,58809	6,58133	6,58809	6,5858	0,00676	-0,00447	0,01123
C7	-0,59941	-0,6016	-0,60979	6,59941	6,60979	6,6016	0,01038	-0,00219	0,01257
C11	-0,02292	-0,04785	-0,04627	6,02292	6,04627	6,04785	0,02335	-0,02493	0,04828
O14	-0,60756	-0,53592	-0,060371	8,60756	8,06037	8,53592	-0,54719	0,07164	-0,618829
C15	-0,0186	-0,04184	-0,03483	6,0186	6,03483	6,04184	0,01623	-0,02324	0,03947
O18	-0,5862	-0,55814	-0,57376	8,5862	8,57376	8,55814	-0,01244	0,02806	-0,0405
C19	-0,01975	-0,05625	-0,03588	6,01975	6,03588	6,05625	0,01613	-0,0365	0,05263
C22	-0,06767	0,01507	-0,0644	6,06767	6,0644	5,98493	-0,00327	0,08274	-0,086601
C23	-0,17732	-0,16307	-0,32613	6,17732	6,32613	6,16307	0,14881	0,01425	0,13456
C24	-0,17171	-0,16614	-0,26619	6,17171	6,26619	6,16614	0,09448	0,00557	0,08891
C25	-0,28671	-0,25489	-0,37679	6,28671	6,37679	6,25489	0,09008	0,03182	0,05826
C26	-0,23603	-0,19821	-0,37027	6,23603	6,37027	6,19821	0,13424	0,03782	0,09642
C27	0,33114	0,33688	0,30566	5,66886	7,69434	5,66312	0,02548	0,00574	0,01974
O28	-0,56789	-0,51557	-0,57758	8,56789	8,57758	8,51557	0,00969	0,05232	-0,04263
C29	-0,04976	-0,07665	-0,06427	6,04976	6,06427	6,07665	0,01451	-0,02689	0,0414
C32	0,13988	0,11551	0,1271	5,86012	5,8729	5,88449	0,01278	-0,02437	0,03715
O34	-0,74463	-0,72078	-0,75357	8,74463	8,75357	8,72078	0,00894	0,02385	-0,01491
C35	-0,1998	-0,24308	-0,21627	6,1998	6,21627	6,24308	0,01647	-0,04328	0,05975
N38	-0,68835	-0,42418	-0,6842	7,68835	7,6842	7,42418	-0,00415	0,26417	-0,26832
C40	0,01367	-0,02397	0,00431	5,98633	5,99569	6,02397	0,00936	-0,03764	0,047
C42	-0,59343	-0,58666	-0,60512	6,59343	6,60512	6,58666	0,01169	0,00677	0,00492
C46	-0,57129	-0,58119	-0,57822	6,57129	6,57822	6,58119	0,00693	-0,0099	0,01683

From the data analysis, it appears that the $\mathbf{C_{23}}$ and $\mathbf{N_{38}}$ atoms have the highest Fukui function values of the inhibitor $\boldsymbol{f^+_{C23}}$ **= 0,14881** and f^-_{N38} = **0,26417**.This allows us to deduce that the nucleophilic attacks take place around the carbon atom $\mathbf{C_{23}}$ (center of nucleophilic attack, included in the LUMO density zone) because it has the greatest values of $f_k{}^+$ and also having the largest value of $\Delta fk(r) > 0$. As for the electrophilic attacks, they occur around the nitrogen atom N38 (center of electrophilic attack, included in the HOMO density zone) because it has the greatest values of $f_k{}^-$ and of $\Delta(r) < 0$ in absolute value

Conclusion

The following conclusions can be drawn from this study:

1. Bisoprolol acts as a good inhibitor of copper corrosion in 1M nitric acid.
2. The inhibition efficiency is concentration and temperature dependent.
3. Bisoprolol adsorbs to copper according to the modified Langmuir isotherm.
4. Calculated thermodynamic parameters related to adsorption and activation show the existence of two types of adsorption (chemisorption is predominant).
5. The chemical quantum parameters confirm the inhibition efficiency of bisoprolol.
6. Condensed Fukui functions show the nucleophilic and electrophilic sites in the molecule.

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