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Inhibition Effect of Tenoxicam on Copper Corrosion in HNO_3: Experimental Study and DFT

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Abstract Tenoxicam was examined as a copper corrosion inhibitor in 1M nitric acid solution using the mass loss technique and quantum chemical studies, based on density functional theory (DFT) at the B3LYP level with the base B3LYP/6-31G(d). The inhibitory efficiency of the molecule increases with increasing concentration and temperature. The adsorption of the molecule on the copper surface follows the modified Langmuir model. The thermodynamic functions related to the adsorption and the activation processes were calculated and discussed. The calculated quantum chemical parameters correlated to the inhibition efficiency are the highest occupied molecular orbital energy (EHOMO), the lowest unoccupied molecular orbital energy (ELUMO), the HOMO-LUMO energy gap, hardness (η), softness (S), the dipole moment (μ), the electron affinity (A), the ionization energy (I), the absolute electronegativity (χ), the fraction (ΔN) of electrons transferred from (MBT) to copper and the electrophilicity index (ω). The local reactivity was analyzed through the condensed Fukui function and condensed softness indices to determine the nucleophilic and electrophilic attack sites. There is good agreement between the experimental and theoretical results.

Keywords: *Tenoxicam, corrosion inhibition, copper, density functional theory (DFT), mass loss technique*

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1. Introduction

Corrosion [1,2] is the degradation of a material by chemical or electrochemical reaction in the presence of an aggressive environment. It occurs in variable environments (industrial, urban, rural).

The consequences are important in various fields and in particular in industry: production stoppage, replacement of corroded parts, accidents and risks of pollution are frequent events with sometimes heavy economic impacts [3]. Corrosion is a topic that deserves further research in order to understand how the degradation affects our life.

Copper [4,5] is one of the most used metals in the industry. It is easily stretched, molded and shaped. It is resistant to corrosion and conducts heat and electricity efficiently. Copper is nowadays a material of choice for a variety of domestic, industrial and high-technology applications. Copper is a relatively noble metal, but it is well-known [6,7,8] that it readily dissolves in nitric acid solutions, for example, in the case of some activities in the fabrication of electronic devices. This situation has induced a great deal of research on copper corrosion inhibition.

One of the most important methods in protection of copper against corrosion is the use of organic inhibitors [9,10,11,12] containing polar groups including nitrogen, sulphur and oxygen and heterocyclic compounds [13-16] with polar functional groups and conjugated double bonds. The inhibitory action of these organic compounds is attributed to their interactions with the copper surface via their adsorption. Polar functional groups [17] are regarded as the reaction centre that stabilizes the adsorption process. In general, the adsorption of an inhibitor on a metal surface [18] depends on the nature and the surface of the metal, the adsorption mode, the molecular structure and the type of the electrolyte solution. However, the rigid rules on environmental protection recommend the use of inhibitors that are very little toxic, eco-friendly and

biodegradable [19,20,21]. In the course of this work, we made the choice to use Tenoxicam which is a therapeutic molecule (anti-inflammatory) and which meets well the requirements of the new international guidelines on environmental protection.

Many techniques can be used to study corrosion inhibition and mechanisms:

Experimentally, gravimetric measurement [22] makes possible to easily determine the speed of corrosion over a relatively long period of time so that the mass loss (link to the inhibition efficiency) induced by the dissolution can be determined with sufficient precision.

Theoretically, understanding the mechanisms of corrosion and corrosion inhibition is therefore a real challenge for research today. In order to get information on the corrosion mechanism, DFT calculations [23,24,25] are made to illustrate the molecular structures and behaviours of corrosion inhibitors. Various quantum chemical parameters [26,27,28] can then be obtained to elucidate the adsorption and corrosion inhibition behaviours of the organic molecules. DFT calculations allow gaining insight into the mechanisms by which inhibitors added to aggressive environments retard the metal-environment interaction.

The main objective of this work is to study the behavior of Tenoxicam, a nonsteroidal anti-inflammatory drug with analgesic and antipyretic properties and its efficiency towards the corrosion of copper inhibitor in 1M nitric acid solution.

2. Materials 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 96% purity.

2.2. The Molecule Studied

Tenoxicam belongs to a class of medicines called non-steroidal anti-inflammatory drugs or NSAIDs. It is used to relieve inflammation, swelling, stiffness and pain associated with rheumatoid arthritis, osteoarthritis, ankylosing spondylitis. The tested molecule of Tenoxicam (Figure 1) was purchased from Sinopharm Chemical Reagent Co Ltd.

This work, which is a contribution to the study of metal corrosion inhibition in acidic media, aims to study the behaviour of Tenoxicam towards copper corrosion in 1M nitric acid. $C_{13}H_{11}N_3O_4S_2$.

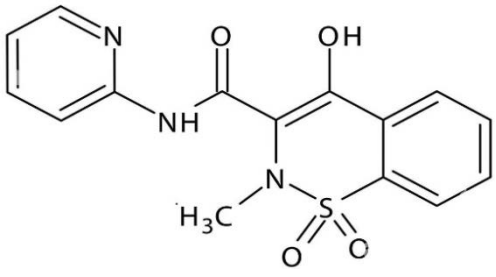

Figure 1. Molecular structure of Tenoxicam.

2.3. Solution

An analytical grade 65% nitric acid solution from Merck was used to prepare the aqueous corrosive solution and acetone of purity 99.5% from Sigma Aldrich for sample surface cleaning. All the chemicals were of analytical grade, so they were used without further purification.

The solution was prepared by diluting the commercial nitric acid solution with ultrapure water. The blank was a 1 M HNO_3 solution. The Tenoxicam solutions prepared were of concentrations 0,01 mM; 0,05 mM; 0,1 mM and 0,5 mM.

2.4. Mass Loss Method

The mass loss method [29,30,31] is one of the most used methods of metal corrosion inhibition assessment due to its simplicity and reliability of measurement. The copper samples were cleaned with emery paper, dipped in acetone, removed and dried before use. They were weighed before and after immersion in 50 mL of the acidic solution with or without Tenoxicam. The tests were repeated three times for each solution, at a given temperature and the mean value was recorded. 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:

$$W = \frac{m_1 - m_2}{St} \quad (1)$$

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

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

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.

2.5. Quantum Calculations

Density functional theory (DFT) calculations were carried out involving various steps including a graphical representation of the geometry of the molecule using the Gaussview visualization interface, and the application of a theoretical method (DFT) implemented in the commercial software Gaussian. For our study, the geometrical optimization of our molecule was performed using the Density Functional Theory (DFT) method with the B3LYP functional [32] and the 6-31G (d) basis, which led toatotal energy of the studied molecule (Tenoxicam) with a good precision with an acceptable CPU time. The software GaussView 5.0 [33] was used to represent the 3D structure and visualize the molecule under study. The calculations were performed with the Gaussian 09 W software [34]. The relevant parameters were calculated to describe the molecule-metal interactions.

The molecular parameters as HOMO and LUMO energies and dipole moment(μ) were obtained. Many other parameters have been deduced from the first ones. So, we determined the energy gap (ΔE), the electron affinity (A), the ionization potential (I), the Chemical hardness (η), the chemical softness (S), the electronegativity (χ), the chemical potential (μP) and the electrophilicity index (ω). The expressions of these parameters are given below:

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (4)$$

$$I = -E_{HOMO} \quad (5)$$

$$A = -E_{LUMO} \quad (6)$$

$$\chi = -\mu_P = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (7)$$

$$\chi = \frac{I + A}{2} \quad (8)$$

$$\eta = \frac{I - A}{2} \quad (9)$$

$$\Delta N = \frac{\phi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})} \quad (10)$$

$$S = \left(\frac{\partial N}{\partial \mu_P}\right)_{v(r)} \quad (11)$$

$$\omega = \frac{\mu_P^2}{2\eta} \quad (12)$$

The local reactivity of the molecule under study can be analyzed by means of the fused Fukui indices. Condensed functions indicate the atoms in a molecule that tend to donate (nucleophilic character) or accept (electrophilic character) an electron or electron pair. The nucleophilic and electrophilic functions can be calculated using the finite difference approximation as follows:

$$f_k^+ = q_k(N+1) - q_k(N) \quad (13)$$

$$f_k^- = q_k(N) - q_k(N-1) \quad (14)$$

In equations (13) and (14), q_k is the gross charge of atom k in the molecule and N is the number of electrons.

3. Results and Discussion

Effect of Tenoxicam on copper corrosion: The corrosion rate, inhibition efficiency and surface coverage were calculated using the following equation (1-3). Figure 2 and Figure 3 show the evolution of corrosion rate and inhibition efficiency as a function of temperature and Tenoxicam concentration, respectively.

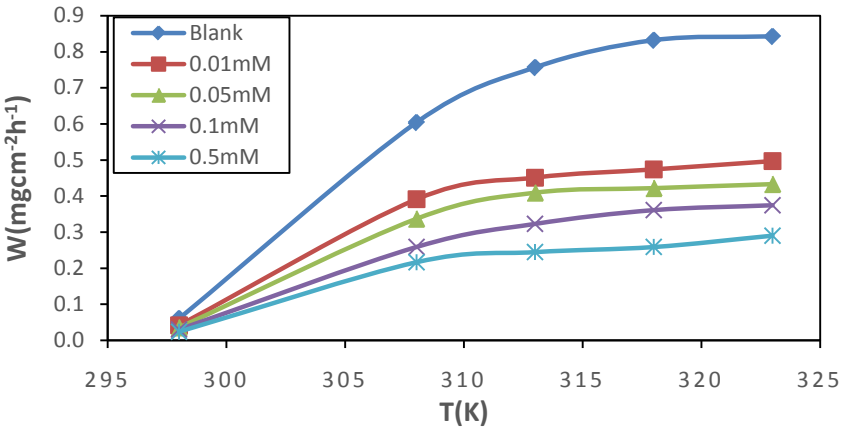

Figure 2. Corrosion rate versus temperature in absence and presence of Tenoxicam

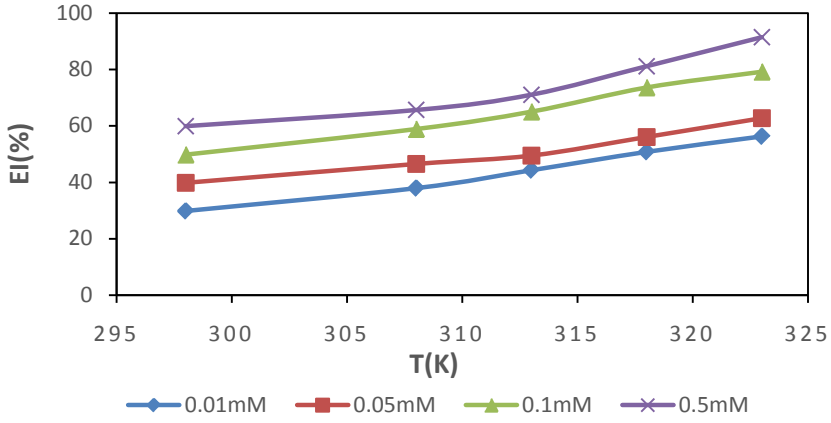

Figure 3. Inhibition efficiency versus temperature for different concentrations in Tenoxicam

Figure 3 shows that the inhibitory efficiency of Tenoxicam 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- Tenoxicam complex film (the vacant d-orbitals of the Cu^{2+} ions receive electrons from the Tenoxicam molecules). This leads to an increase in inhibitory efficiency as the temperature increases.

Adsorption isotherms and adsorption thermodynamic functions: The adsorption on the metal surface is the primary step in the action of inhibitors in acidic solutions. Adsorption isotherm is a model used in representing the relationship between the amount of adsorbate (molecules) adsorbed onto the metal surface at a constant temperature. In order to obtain the isotherm, the surface coverage values (θ) were represented as a function of the inhibitor concentration for a given temperature. It is necessary to determine empirically which isotherm fits best to the adsorption of the inhibitor. Several adsorption isotherms (Langmuir, El-Awady, Temkin, and Freundlich) were tested. The Langmuir isotherm was found to provide the best description of the adsorption of the studied molecule. The equation of this isotherm is given below:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (15)$$

In this equation C_{inh} is the inhibitor concentration, θ is the fraction of surface covered and K_{ads} is the adsorption equilibrium constant. Table 1 gives the equations and the correlation coefficient of the straight lines. Figure 4 gives the plots of $\frac{C_{inh}}{\theta}$ versus C_{inh}.

Table 1. Equation and correlation coefficient of the Langmuir model

T(K)	Equations	R^2
298	$C_{inh}/\theta = 1.5977C_{inh} + 0.0381$	0,9983
308	$C_{inh}/\theta = 1.4553C_{inh} + 0.0373$	0,997
313	$C_{inh}/\theta = 1.3173C_{inh} + 0.0275$	0,9978
318	$C_{inh}/\theta = 1.2291C_{inh} + 0.0235$	0,9981
323	$C_{inh}/\theta = 1.0397C_{inh} + 0.0227$	0,9979

The plots are straight lines with correlation coefficient near unity. However, the slopes are different from unity, which does not allow the Langmuir isotherm to be applied rigorously. Therefore, the modified Langmuir isotherm known as Villamil isotherm [35] is used. The equation of this isotherm is:

$$\frac{C_{inh}}{\theta} = \frac{n}{K} + nC_{inh} \qquad (16)$$

The change in adsorption enthalpy ΔG^0_{ads} was calculated using the following equation:

$$\Delta G^0_{ads} = -RTln(55,5K_{ads}) \qquad (17)$$

In equation (17), R is the perfect gas constant, T is the absolute temperature and 55.5 is the concentration in ($mol.L^{-1}$) of water in the solution.

The changes in enthalpy (ΔH^0_{ads}) and entropy (ΔS^0_{ads}) are related tothe change in free adsorption enthalpy by the basic equation below:

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads} \qquad (18)$$

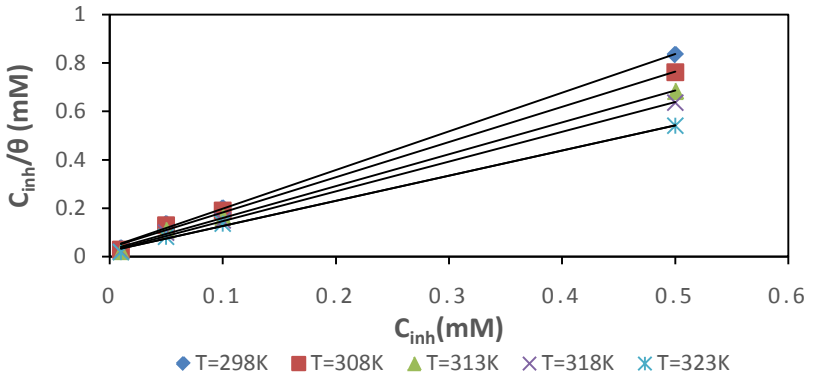

Figure 4. Langmuir adsorption isotherm for Tenoxicam on copper surface

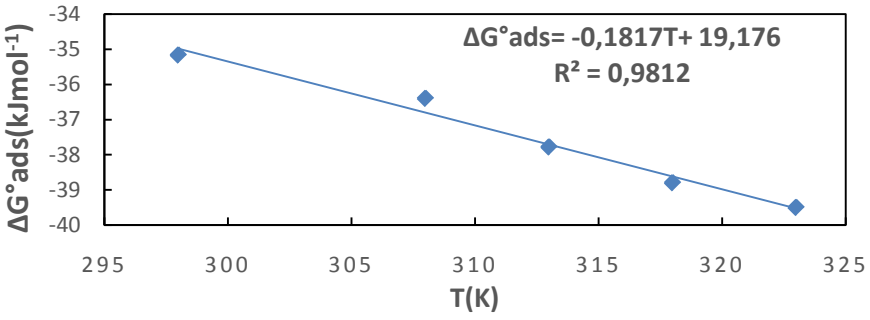

Figure 5. Change in free adsorption enthalpy versus temperature

Figure 5 presents the plot of ΔG^0_{ads} versus temperature. The plot is a straight line with a slope ($-\Delta S^0_{ads}$) and an intercept (ΔH^0_{ads}). The obtained values are listed in Table 2.

Table 2. Values of the adsorption thermodynamic functions

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	26247	-35.161	19.176	18.17
308	26810	-36.395		
313	36360	-37.779		
318	42553	-38.798		
323	44053	-39.501		

The negative values of the free adsorption enthalpy show the spontaneous character of the adsorption phenomenon. 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 [36] to the desorption of water molecules.

The values of ΔG^0_{ads} range from -40 kJ.mol^{-1} to -20 kJ.mol^{-1}, showing that thermodynamic parameters point toward both physisorption and chemisorptions [37]. 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 isotherms.

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

$$\log\left(\frac{1}{1-\theta}\right) = \log K_{AE} + b\log C_{inh} \qquad (19)$$

Where C_{inh} is the concentration of the adsorbate, K_{AE} and b are the isotherm parameters. The evolution of the parameter b determines [38] the type of adsorption: decrease in values of this parameter indicates physisorption, while increase or fairly constant values signifies chemisorption. Figure 6 gives the plots of the isotherm.

All the isotherm parameters are listed in Table 3.

Table 3. Adejo-Ekwenchi isotherm parameters

T(K)	b	log K_{AE}	K_{AE}	R^2
298	0.1467	0.4364	2.7315	0,9739
308	0.1745	0.5348	3.4261	0,9779
313	0.2085	0.6162	4.1324	0,9688
318	0.2637	0.8104	6.4625	0,9777
323	0.3631	1.0626	11.5505	0,9779

From Table 3, it is clear that the parameters and K_{AE} increase for temperatures range from T = 298K to 323K. which shows that the adsorption of Tenoxicam on copper is dominated by chemisorption [38].

3.1. Activation Parameters of the Corrosion Process

The corrosion rates were evaluated at different temperatures in the absence and presence of Cefepime; they were used to calculate the activation energy of the metal dissolution. The Arrhenius equation [39] and the transition state equation [40] were used to calculate the apparent activation energy (E_a), the change in activation enthalpy (ΔH^*_a) and change in activation entropy (ΔS^*_a)

$$logW = logA - \frac{E_a}{2{,}303RT} \qquad (20)$$

$$\log\left(\frac{W}{T}\right) = \left[\log\left(\frac{R}{\aleph h}\right) + \frac{\Delta S^*_a}{2{,}303R}\right] - \frac{\Delta H^*_a}{2{,}303RT} \qquad (21)$$

In these equations, R is the universal gas constant, h is the Planck constant and $\aleph$ is the Avogadro number. Figure 7 and Figure 8 give the plots of and that of log ($/T$) versus 1/T.

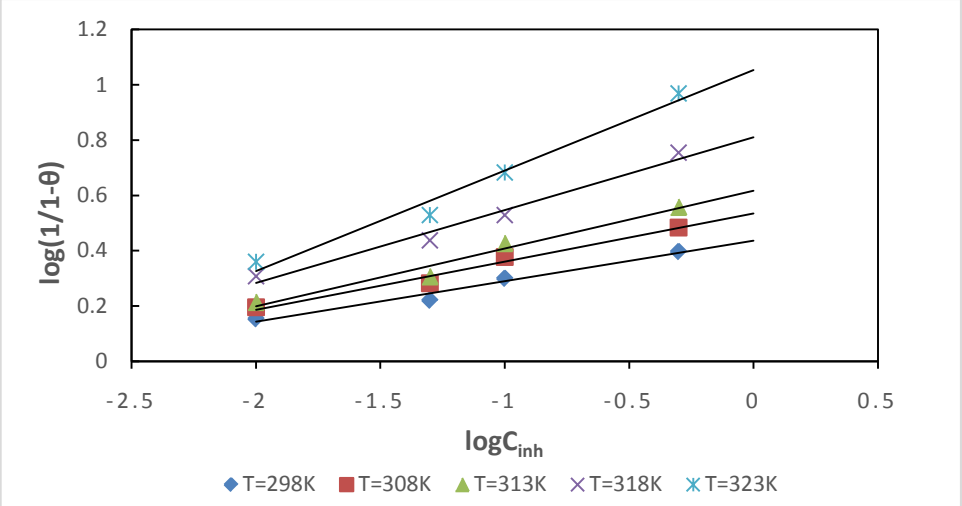

Figure 6. Adejo-Ekwenchi isotherm for different temperatures

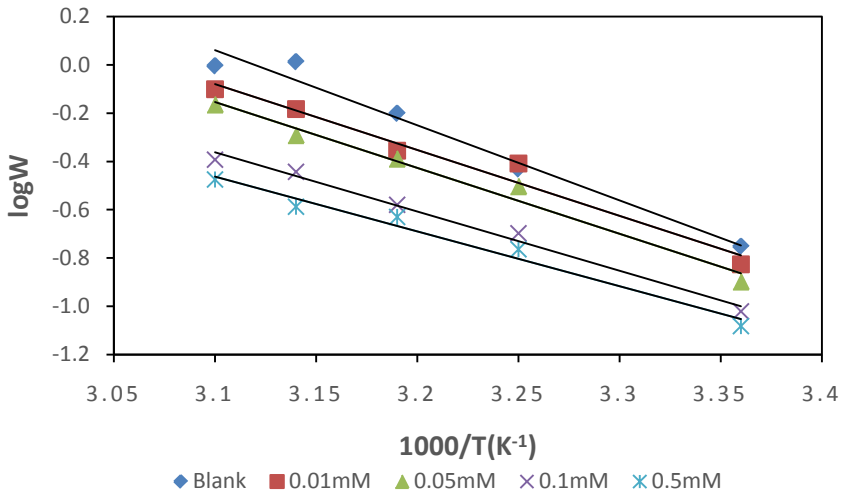

Figure 7. Arrhenius plots for copper corrosion in 1M HNO_3

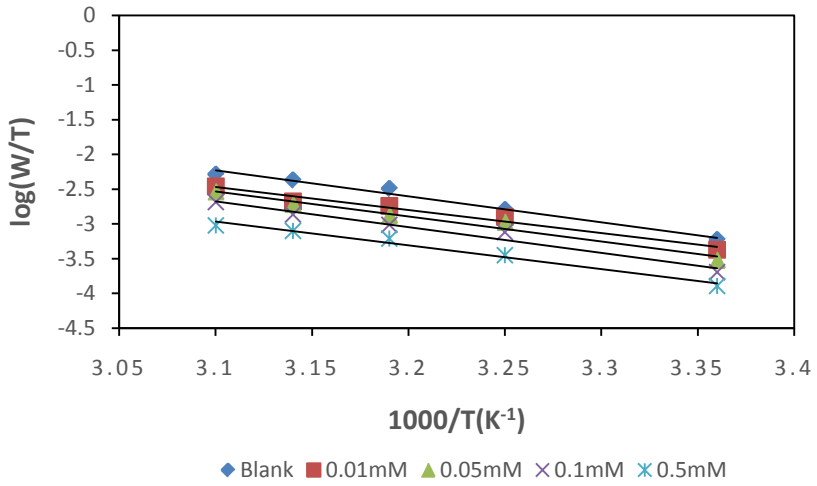

Figure 8. Transition state plots for copper corrosion in 1M HNO_3

The parameters of the dissolution of copper in the absence or presence of Tenoxicam in the studied environment are listed in Table 4.

Table 4. Activation parameters of the corrosion of copper in 1 M HNO_3 in the absence and presence of Tenoxicam

C_{inh} (mM)	$E_a(kJ.mol^{-1})$	$\Delta H_a^*(kJ.mol^{-1})$	$\Delta S_a^*(J.mol^{-1}.K^{-1})$
Blank	59.609	71,559	-18,393
0.01	52.182	63,333	-48,548
0.05	52.218	68,97	-32,258
0.1	46.968	70,833	-29,259
0.5	43,416	65,313	-51,916

The activation energy in the absence of Tenoxicam (Blank) is higher than the activation energies in its presence; this would indicate according to the literature [41] that chemisorption is predominant.

The obtained values of ΔH_a^* are in good agreement with the values calculated from the equation below:

$$\Delta H_a^* = E_a - RT \quad (22)$$

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 [42] some organization during the formation of the activated complex.

3.2. Theoretical Studies

3.2.1. Global Molecular Parameters

Global parameters of Tenoxicam have been calculated, using Gaussian 09, with B3LYP/6-31G (d) method. All these parameters are listed in Table 5.

Table 5. Global molecular parameters of Tenoxicam by B3LYP/6-31 G (d)

Parameter	Value	Parameter	Value
E_{HOMO} (eV)	-6.276	χ (eV)	4.343
E_{LUMO} (eV)	-2.410	η (eV)	1.933
ΔE (eV)	3.866	S $(eV)^{-1}$	0.517
μ (Debye)	3.4580	ΔN	-0.016
I (eV)	6.276	ω (eV)	4.878
A (eV)	2.410	E_T	-1763.46

The parameter EHOMO (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 Tenoxicam, with EHOMO (-6.276 eV) can be considered [43] as a good electrons donor. On the other hand, ELUMO, 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 (-2.410 eV), indicating [43] a good acceptor capacity.

The energy gap HOMO-LUMO is an important parameter that need to be considered. Lower values of this energy [44] lead to higher reactivity tendency, indicating good inhibition efficiency. For the studied molecule, the value of the energy gap (ΔE = 3.866 eV) can be considered [45,46] as low when comparing to values in the literature.

The overall softness (s) and the overall hardness (η) are also important reactivity parameters that provide information on the likely ability of a molecule to interact with a metal surface [47].

They measure molecular stability as well as molecular reactivity. A hard molecule has a large energy gap and a soft molecule has a small energy gap. A good inhibitor has a high softness value and a low hardness value (low ΔE). The results show that Tenoxicam has low hardness values (η=1.933eV) and therefore a high softness [s = 0.517 $(eV)^{-1}$] compared to those found in the literature [48]. This value reflects the experimental results.

The ionization energy is also an important descriptor of the chemical reactivity of atoms and molecules. A high ionization energy indicates high stability while a low value is associated with high reactivity of atoms and molecules [49].

In our work, the low ionization energy (6.276 eV) surely explains the good inhibitory power of Tenoxicam compared to those found in the literature [48].

The dipole moment (μ) result from non-uniformity in the charges distribution in the molecule. Though this parameter is important, there is [50] irregularities in the correlation between it and the inhibition efficiency. In our case, the value of this parameter is high (μ=3.4580 Debye). According to some authors [48,51], the ability of a molecule to adsorb to the surface of a metal is all the greater as its dipole moment is high.

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 study, the value of the electrophilicity index (ω =4.878 eV) indicates that Tenoxicam has the ability to accept electrons from copper [48].

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 [52] is given by:

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2\left(\eta_{Cu} + \eta_{inh}\right)} \quad (23)$$

Where χCu, ηCu, χinh and ηinh are respectively the absolute electronegativity and hardness of copper and the inhibitor. We use the theoretical value of χCu = 4.98 eV/ [52] and ηCu = 0 [52] for the calculation of the number of electrons transferred. The negative value of ΔN(-0.016) indicates that the molecule have rather tendency to receive electrons from the metal.

3.2.2. Local Reactivity Parameters

Local reactivity was analyzed by means of Fukui functions and dual descriptor in order to assess the nucleophilic and electrophilic attack centre.

It has been proved [53,54] that the dual descriptor described well the reactivity, combining Fukui functions. So, the condensed dual descriptor over atomic sites, indicates a process driven by a nucleophilic attack on atom k when Δfk > 0 (atom k reacts as an electrophilic species) and a process driven by an electrophilic attack when Δfk < 0 (atom k reacts as a nucleophilic species).

Figure 9 and Figure 10 give respectively the structure and the HOMO and LUMO orbitals of Tenoxicam while Table 6 presents Fukui and dual functions.

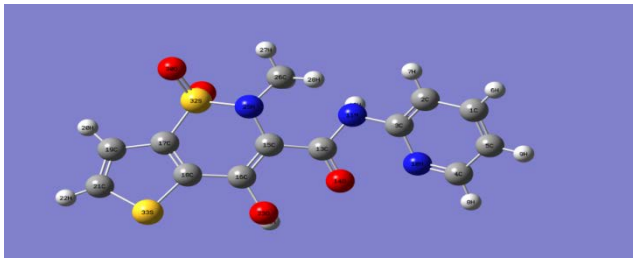

Figure 9. Structure of Tenoxicam by B3LYP/6-31 G(d)

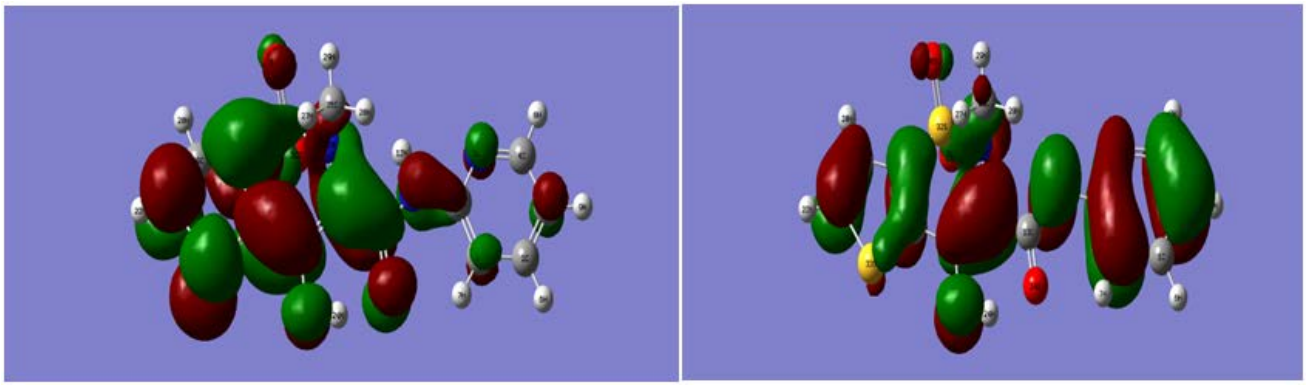

Figure 10. HOMO (left) and LUMO (right) orbitals of Tenoxicam by B3LYP/6-31G (d)

Table 6. Fukui and dual functions of atoms in Tenoxicam, obtained using Mulliken charges

Atom	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	Δf_k
1 C	-0,120048	-0,114189	-0,096354	-0,005859	-0,017835	0,011976
2 C	-0,159924	-0,150373	-0,170976	-0,009551	0,020603	-0,030154
3 C	0,493286	0,494369	0,489866	-0,001083	0,004503	-0,005586
4 C	0,039671	0,044899	0,047278	-0,005228	-0,002379	-0,002849
5 C	-0,158142	-0,141804	-0,132359	-0,016338	-0,009445	-0,006893
6 H	0,112111	0,148561	0,182828	-0,03645	-0,034267	-0,002183
7 H	0,180465	0,189827	0,163805	-0,009362	0,026022	-0,035384
8 H	0,10956	0,147439	0,1809	-0,037879	-0,033461	-0,004418
9 H	0,097776	0,140162	0,179715	-0,042386	-0,039553	-0,002833
10 N	-0,511383	-0,499404	-0,439396	-0,011979	-0,060008	0,048029
11 N	-0,717536	-0,712005	-0,692262	-0,005531	-0,019743	0,014212
12 H	0,35686	0,373895	0,365653	-0,017035	0,008242	-0,025277
13 C	**0,602161**	**0,664672**	**0,667164**	**-0,062511**	**-0,002492**	**-0,060019**
14 O	-0,662326	-0,607622	-0,52922	-0,054704	-0,078402	0,023698
15 C	**0,056621**	**0,105375**	**0,235375**	**-0,048754**	**-0,13**	**0,081246**
16 C	0,344145	0,367619	0,381381	-0,023474	-0,013762	-0,009712
17 C	-0,191153	-0,16065	-0,154003	-0,030503	-0,006647	-0,023856
18 C	-0,20326	-0,183455	-0,182423	-0,019805	-0,001032	-0,018773
19 C	-0,104762	-0,106248	-0,090021	0,001486	-0,016227	0,017713
20 H	0,134134	0,186388	0,229176	-0,052254	-0,042788	-0,009466
21 C	-0,372581	-0,342266	-0,317985	-0,030315	-0,024281	-0,006034
22 H	0,128114	0,19438	0,247208	-0,066266	-0,052828	-0,013438
23 O	-0,683128	-0,635565	-0,567047	-0,047563	-0,068518	0,020955
24 H	0,434461	0,458121	0,489234	-0,02366	-0,031113	0,007453
25 N	-0,647138	-0,659971	-0,644321	0,012833	-0,01565	0,028483
26 C	-0,303098	-0,322402	-0,365892	0,019304	0,04349	-0,024186
27 H	0,148625	0,163467	0,250101	-0,014842	-0,086634	0,071792
28 H	0,149888	0,176217	0,230294	-0,026329	-0,054077	0,027748
29 H	0,17293	0,208416	0,215535	-0,035486	-0,007119	-0,028367
30 O	-0,57596	-0,526299	-0,457121	-0,049661	-0,069178	0,019517
31 O	-0,522725	-0,485936	-0,427555	-0,036789	-0,058381	0,021592
32 S	1,187416	1,242053	1,252085	-0,054637	-0,010032	-0,044605
33 S	0,18494	0,342329	0,45934	-0,157389	-0,117011	-0,040378

Analysing the dual functions, one can see that in Tenoxicam, the probable electrophilic attack centre is C (13) with $\Delta fk < 0$, while the probable nucleophilic attack centre is C (15) with $\Delta fk > 0$.

4. Conclusion

Mass loss and theoretical method were used to evaluate the copper corrosion inhibition by Tenoxicam in 1M HNO_3. The main finding of this study are as follows:

- Tenoxicam acts a good inhibitor for copper corrosion in 1M HNO_3 and its Inhibition efficiency increases with increasing concentration and temperature.
- The adsorption of Tenoxicam on copper surface obeys the modified Langmuir adsorption isotherm or Villamil model and is a spontaneous, exothermic process accompanied by an increase in entropy.
- The adsorption process is dominated by chemisorption.
- Thermodynamic activation parameters indicate an exothermic dissolution process.
- The Fukui functions and the dual descriptor have proved that C(15) and C(13) are respectively the probable sites of nucleophilic and electrophilic attack.

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