

Thermodynamic and quantum chemistry characterization of adsorption of 2-hydroxymethylbenzimidazole (HMBI) and 2-thiomethylbenzimidazole (TMBI) during copper corrosion inhibition in 1M nitric acid.

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Summary: This work is centered on the study of the corrosion inhibition of copper in 1M HNO₃ by 2-hydroxymethylbenzimidazole (HMBI) and 2-thiomethylbenzimidazole (TMBI). The inhibition efficiencies obtained by weight loss technique show that these compounds are good inhibitors. The Langmuir adsorption isotherm was found to be closed to the adsorption behavior of the studied compounds. The adsorption of these compounds has been tested thermodynamically and found to be of both physisorption and chemisorption. Furthermore, some activation thermodynamic parameters such as ΔH^* , ΔS^* have been estimated. In addition, a trial of finding a quantitative relationship between the inhibition efficiency and the electronic properties of the molecules was carried using Gaussian 03W at density functional theory (DFT) level with B3LYP exchange correlation functional for 6-31G(d) and 6-311G(d,p) basis sets. Theoretical results are in accordance with the experimental data to good extend.

Key words: Corrosion Inhibitor, adsorption isotherm, enthalpy, entropy, dipole moment, theoretical calculation.

Caractérisation de l'adsorption du 2-hydroxyméthylbenzimidazole(HMBI) et du 2-thiométhylbenzimidazole (TMBI) sur le cuivre en milieu acide nitrique 1M par analyse de certaines grandeurs thermodynamiques et de chimie théorique.

Résumé : Ce travail porte sur l'étude de l'inhibition de la corrosion du cuivre en milieu acide nitrique 1M par le 2- hydroxyméthylbenzimidazole (HMBI) et le 2- thiométhylbenzimidazole (TMBI). Les efficacités inhibitrices obtenues par gravimétrie montrent que ces composés sont de bons inhibiteurs de la corrosion du cuivre dans le milieu étudié. Ces études montrent aussi que ces composés s'adsorbent sur le cuivre selon le modèle de l'isotherme de Langmuir. Les grandeurs thermodynamiques liées à l'adsorption de ces molécules indiquent que les interactions entre ces molécules et la surface métallique sont de natures physique et chimique. Nous avons, en outre, déterminé les grandeurs thermodynamiques (ΔH^* , ΔS^*) liées à la dissolution du cuivre. Des études théoriques supplémentaires ont été menées afin de déterminer les corrélations entre les efficacités inhibitrices de ces molécules et leurs propriétés électroniques. Le logiciel GAUSSIAN 03 W a permis de réaliser les calculs soutenus par la théorie de la fonctionnelle de densité (DFT/ B3LYP) avec les bases 6-31G(d) et 6-311G (d,p). Un bon accord entre les résultats théoriques et expérimentaux a été trouvé.

Mots-clés: Inhibiteur de corrosion, isotherme d'adsorption, enthalpie, entropie, moment dipolaire, calcul théorique.

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1. Introduction

Acids such as hydrochloric acid ^[1], nitric acid and sulfuric acid ^[2] are generally used for the removal of metal scale and rust in many industrial processes. Because of the aggressiveness of these acid solutions, inhibitors are widely used to reduce the corrosion on metallic materials ^[3-5]. Addition of inhibitors remains one of the necessary procedures used to protect metals and alloys against attack in many industrial environments. Therefore the development of corrosion inhibitors based on organic compounds containing nitrogen, sulfur and oxygen atoms are of growing interest in the field of corrosion and industrial chemistries as corrosion poses a serious problem to the service life time of metals and alloys in the industry ^[6]. The efficiency of these inhibitors is related to the nature of the metal, the state of the metallic surface, chemical composition and the structure of the inhibitors.

In order to evaluate compounds as corrosion inhibitors and design novel inhibitors with established aim, recently, more and more researchers focus on the relationship between the structural molecular properties and corrosion inhibition efficiencies. Different species of organic compounds are investigated for their inhibiting behaviors and their molecular structures are also studied by quantum chemical method to seek for some useful information determining their inhibition. Factors affecting the adsorption of these molecules, such as functional groups, steric effects, electron density at donor's atoms and orbital character of donating electrons have been considered and discussed in terms of their inhibiting abilities. Many corrosion inhibitors used in aqueous heating and cooling systems are generally toxic ^[7]. This toxic property limits the field of their applications. However there is a great demand for non-toxic corrosion inhibitors. The compounds studied in this work are non-toxic in nature ^[8].

Recently, quantitative structure activity relationship (QSAR) has been a subject of intense interest in many disciplines of chemistry. The development of semi-empirical quantum chemical calculations emphasizes the scientific approaches involved in the selection of inhibitors by correlating the experimental data with quantum chemical properties. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), charges on reactive center, dipole moment (μ) and conformations of molecules have been used to achieve the appropriate correlations.

The aim of this work is to estimate the thermodynamic parameters of adsorption and those of activation during copper corrosion inhibition in 1M HNO₃. The work is also focus on the relationship between quantum chemical calculations and experimental inhibition efficiencies of the studied compound by determining for these molecules, quantum chemical parameters such as the energy of the highest occupied molecular orbital (E_{HOMO}), that of the lower unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO} and the dipole moment (μ).

2. Experimental

• Molecules structures

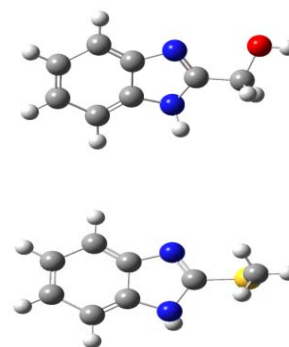


Figure 1: Optimized Chemical structures of 2-hydroxymethylbenzimidazole and 2-thiomethylbenzimidazole.

2- hydroxymethylbenzimidazole (HMBI)
and 2- thiomethylbenzimidazole (TMBI)

have been synthesized in the Laboratory. Their molecular structures have been identified by RMN- ^1H and ^{13}C spectroscopies, mass spectroscopy and X-rays.

• Weight loss measurements

The weight loss measurements were performed with samples of copper in the form of rods measuring 10 mm by 2.2 mm of diameter that were cut from commercial pure copper (Cu 99.5 %).

The corrosive solution of 1M HNO_3 was prepared by dilution of analytical grade 65% HNO_3 from MERCK with bidistilled water. The samples were polished with different emery papers, washed thoroughly with bidistilled water, degreased and dried with acetone. The samples were kept in a desiccator, weighed and immersed in the corrosive medium (50 mL of 1M HNO_3) with or without the tested inhibitors. A water thermostat SELECTA (FRIGITERM) controlled to $\pm 0.5^\circ\text{C}$ maintained the temperatures. After 1 hour, the specimens were removed, rinsed in bidistilled water then kept in a desiccator and then reweighed. All tests were made in aerated solutions and were run triplicate.

3. Results and discussion

3.1 Thermodynamics considerations

3.1.1. Adsorption isotherm

Basic information on the interaction between the inhibitor and the copper surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the fractional coverage values as a function of inhibitor concentration must be obtained. It is well known that θ can be obtained from the corrosion rate [9, 10]:

$$\theta = 1 - \frac{W}{W_0} \quad (1)$$

Where W_0 and W are respectively the corrosion rates of copper in the absence and in the presence of the tested compounds. The values obtained from equation (1) are listed in Table I. Attempts were made to fit these values to various

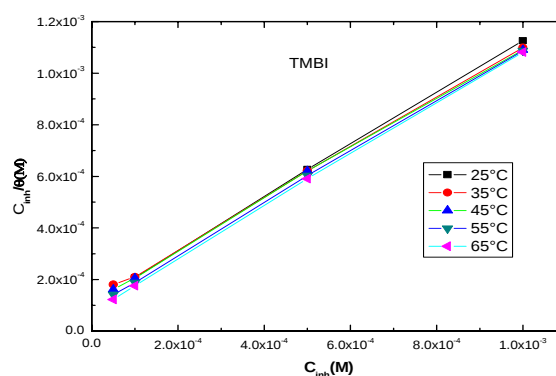
isotherms including Frumkin, Langmuir, Temkin, and Freundlich. Many adsorption isotherms were plotted and the Langmuir adsorption isotherm was found to be the best description of the adsorption behavior of the studied inhibitors.

According to this isotherm, θ is related to the equilibrium adsorption constant (K) and the inhibitor concentration (C_{inh}) via [11].

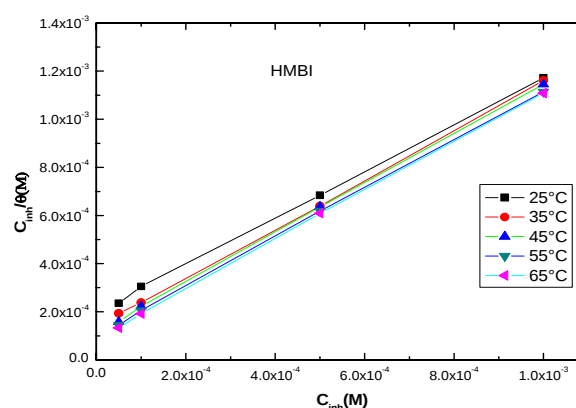
$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K} + C_{\text{inh}} \quad (2)$$

The values of C_{inh}/θ versus the temperature and the concentration are below, registered in Table II.

Figure 2 shows the dependence of C_{inh}/θ as a function of the concentration C_{inh} of TMBI or HMBI.



(a)



(b)

Figure 2: Langmuir's adsorption plots for copper in 1M HNO_3 containing various concentrations of inhibitor at different temperatures.

(a): TMBI (b): HMBI

Table I: Surface coverage values of the tested molecules.

	θ_{TMBI}				θ_{HMBI}			
$C_{inh}(M)$	$5 \cdot 10^{-5}$	10^{-4}	$5 \cdot 10^{-4}$	10^{-3}	$5 \cdot 10^{-5}$	10^{-4}	$5 \cdot 10^{-4}$	10^{-3}
T(K)								
298	0.267	0.484	0.797	0.888	0.213	0.328	0.731	0.853
308	0.277	0.475	0.805	0.910	0.259	0.420	0.782	0.861
318	0.309	0.486	0.805	0.917	0.317	0.450	0.786	0.873
328	0.353	0.531	0.829	0.920	0.348	0.487	0.808	0.898
338	0.407	0.569	0.846	0.925	0.377	0.521	0.821	0.902

Table II: C_{inh}/θ as a function of both temperature and concentration.

	$10^4 * C_{TMBI}/\theta$				$10^4 * C_{HMBI}/\theta$			
$C_{inh}(M)$	$5 \cdot 10^{-5}$	10^{-4}	$5 \cdot 10^{-4}$	10^{-3}	$5 \cdot 10^{-5}$	10^{-4}	$5 \cdot 10^{-4}$	10^{-3}
T(K)								
298	1.873	2.066	6.273	11.261	2.347	3.049	6.840	11.720
308	1.805	2.105	6.211	10.990	1.930	2.381	6.394	11.614
318	1.618	2.058	6.211	10.905	1.577	2.222	6.361	11.454
328	1.416	1.883	6.031	10.869	1.437	2.053	6.188	11.136
338	1.228	1.757	5.910	10.811	1.326	1.919	6.090	11.086

Table III: Values of the equilibrium constant and the energy adsorption versus the temperature.

Compound	K(M ⁻¹)		ΔG_{ads}^0 (kJ.mol ⁻¹)	
	TMBI	HMBI	TMBI	HMBI
T(K)				
298	9176.8	5097.0	-32.54	-31.08
308	8029.5	7304.5	-33.29	-33.05
318	8751.6	8802.9	-34.60	-34.61
328	10754.1	9942.8	-36.25	-36.04
338	13922.2	11413.0	-37.91	-37.52

The obtained plots are linear with correlation coefficients (R^2) almost equal to 1. It is also found that all the values of the slopes are very close to 1, which indicates that the adsorption of inhibitors onto copper surface accords with the Langmuir adsorption isotherm. These results also indicate that there are no interactions among the adsorbed species [12,13]. The equilibrium constant of adsorption is related to the standard free energy of adsorption ΔG_{ads}^0 by:

$$K = \frac{1}{55.5} \cdot \exp\left(-\frac{\Delta G_{ads}^0}{RT}\right) \quad (3)$$

Where R is universal gas constant, T the absolute temperature and 55.5, the value of the concentration of water in the solution in mol.dm⁻³.

The adsorption coefficient and the standard free adsorption energy ΔG_{ads}^0 were

The negative values of ΔG_{ads}^0 indicate a spontaneous adsorption process of TMBI and HMBI on copper [14]. It is generally accepted that for the values of ΔG_{ads}^0 up to - 20kJ.mol⁻¹, the type of adsorption were regarded as physisorption; the inhibition acts due to the electrostatic interactions between the charged molecules and the charged metallic surface, while the values around - 40 kJ.mol⁻¹ or smaller were seen as chemisorption, which is due to the charge sharing or a transfer from the inhibitors molecules to the metal surface to form a covalent bond [15,16]. The values of ΔG_{ads}^0 in our measurements range from -31 to -38 kJ.mol⁻¹: it is suggested that the adsorption of these molecules involves both types of interactions, chemisorption and physisorption.

3.1.2. Effect of temperature on the corrosion rate.

The corrosion reaction can be regarded as an Arrhenius-type process, the rate of which is given by:

$$W = k \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

Where W is the corrosion rate, k the Arrhenius preexponential constant, and E_a the activation energy for the corrosion process which represents the energy necessary for a reactant to possess in order to react. Table 4 shows the variation of the W values with temperature in 1M HNO_3 in the absence and presence of the tested inhibitors, respectively.

Table IV: Variation of the W values with temperature in 1M HNO_3 in the absence and presence of the tested inhibitors

T(K)	1/T ($\times 10^{-3} \text{K}^{-1}$)	$\log W_{\text{Blank}}$	$\log W_{\text{TMBI}}$	$\log W_{\text{HMBI}}$
298	3.356	-0.965	-1.950	-1.797
308	3.247	-0.870	-1.914	-1.726
318	3.144	-0.800	-1.882	-1.696
328	3.049	-0.755	-1.852	-1.644
338	2.958	-0.717	-1.823	-1.601

Figure 3 presents the Arrhenius plots of the logarithm of the corrosion rate versus $1/T$ for copper in 1M HNO_3 in the absence and in the presence of the tested molecules at their optimum concentration ($C_{\text{inh}} = 10^{-3} \text{M}$).

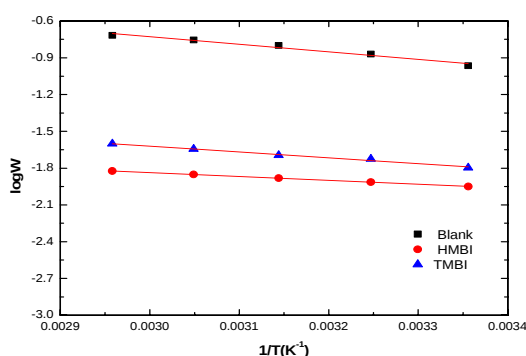


Figure 3: $\log W$ as a function of $1/T$

The calculated values of E_a from the slopes of these straight lines are listed in Table V.

In the presence of the tested molecules, the activation energy E_a decreased, indicating the formation of a chemisorbed film on the metal surface. Similar interpretations can be found in the literature ^[17,18].

3.1.3. Temperature effect and thermodynamic activation parameters

The enthalpy of activation ΔH^* can be obtained from the following relation ^[19]:

$$E_a = \Delta H^* - RT \quad (5)$$

The free activation energy (ΔG^*) which is defined as the difference in the activation energies between the activated state and the initial state of the reacting species is calculated using Eyring's equation ^[19]:

$$K = \left(\frac{k_B T}{h}\right) \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (6)$$

Where K is the rate constant, k_B the Boltzmann's constant, h the Planck's constant and T the absolute temperature. The activation entropy (ΔS^*) is obtained using the equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (7)$$

The thermodynamic activation parameters calculated using the above relations are listed in Table 6.

A comparison of the activated parameters (Tables V and VI) corresponding of the free and the inhibited systems indicates that the corrosion process is enthalpy-controlled. The positive values of ΔH^* reflect the endothermic nature of the copper dissolution process. The negative values of the activation entropy imply that the activated complex in the rate determining step represents an associatively activated process ^[19], meaning that a decrease in disordering

Tableau V: Activation energies for the corrosion of copper in 1M HNO₃ in the absence and the presence of the tested molecules at C = 10⁻³M.

	Blank	HMBI	TMBI
E _a (kJ.mol ⁻¹)	11.8	6.1	9.1

Table V: The thermodynamic activation parameters in 1M HNO₃ in the absence and in the presence of the inhibitors.

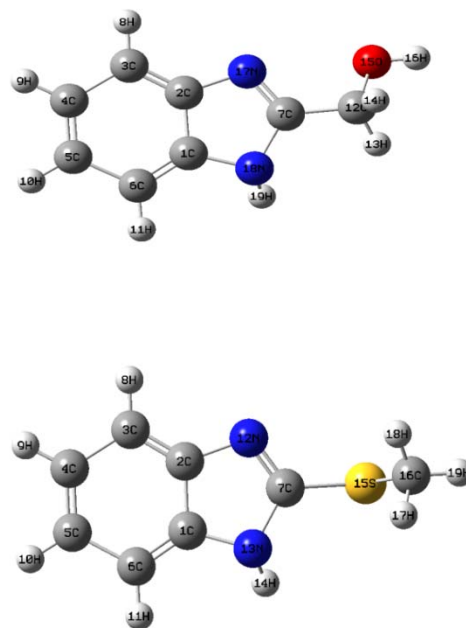
Temperature (K)	TMBI			HMBI		
	ΔG* (kJ.mol ⁻¹)	ΔH* (kJ.mol ⁻¹)	ΔS* (J.mol ⁻¹)	ΔG* (kJ.mol ⁻¹)	ΔH* (kJ.mol ⁻¹)	ΔS* (J.mol ⁻¹)
298	50.3	11.58	-129.2	51.7	8.58	-144.7
308	52.4	11.66	-131.0	52.6	8.66	-142.7
318	54.0	11.74	-132.9	54.0	8.74	-142.3
328	55.2	11.82	-132.2	55.4	8.82	-142.0
338	56.2	11.91	-131.0	56.8	8.91	-141.6

3.2 Quantum chemistry calculations

Quantum chemical calculations have been widely used to study reaction mechanism. They have also proved to be a very important tool for studying corrosion inhibition mechanism [20-22]. In recent times, Density Functional Theory (DFT) has become an attractive theoretical method because it gives exact vital parameters for even huge complex molecules at low cost. Furthermore, by using sophisticated computational tools, we can understand reactivity behavior of hard and soft acid-base (HSAB) theory that provide a systematic way for the analysis of the inhibitor/surface interaction [23].

The problem of relationship between the molecular structure and the inhibition efficiency of the organic inhibitors of corrosion attracts the attention of many investigators [24,25]. Parameters like E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (Lower unoccupied molecular orbital energy), energy gap (ΔE = E_{LUMO} - E_{HOMO}) and molecular dipole moment have been used for correlation with corrosion data.

The geometry of HMBI and TMBI were optimized by the density functional theory (DFT) method level with B3LYP exchange correlation functional, using 6-31G(d) and 6-311G(d,p) basis sets. The optimized

**Figure 4:** Optimized structures with labels and symbols.

All theoretical calculations were performed with the Gaussian 03 W suite of programs; we have determined quantum chemical parameters such as: E_{LUMO}, E_{HOMO}, ΔE = E_{LUMO} - E_{HOMO}, dipole moment μ, ionization potential (I = -E_{HOMO}) and electron affinity (A = -E_{LUMO}) of the studied molecules. The obtained values of I

and A were considered for the calculation of the electronegativity χ and the global hardness η in each of the tested molecule using the following relations ^[26]:

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

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

The fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) (Table VII) was calculated according to Pearson's formula:

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

The idea behind this is that in the reaction of two systems with different electronegativity as a metallic surface and an inhibitor molecule, the following mechanism will take place: the electron flow will happen from the molecule with the low electronegativity towards that of a higher value until the chemical potentials are the same. In order to calculate the fraction of electrons transferred, a theoretical value of electronegativity of bulk copper was used $\chi_{Cu} = 4.98 \text{ eV}$ ^[27] and a global hardness $\eta_{Cu} = 0$ assuming that for a metallic bulk $I = A$ ^[28] because they are softer than the neutral metallic atoms. The calculated parameters are listed in Table VII.

Through these calculations an attempt has been made to correlate corrosion inhibition efficiency (dependent variable) and the set of some independent variables like highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), dipole moment etc.

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between frontier orbitals (HOMO and LUMO) of reacting species [29]. Thus, the treatment of the frontier molecular orbitals separately from the other orbitals is based on the general principles governing the nature of chemical reactions. HOMO is often associated with the electron donating ability of a molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer ^[30]. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of E_{LUMO} , the more probable it is that the molecule would accept electrons ^[30]. Low values of the energy band gap (ΔE) give good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low ^[30].

Table VII: The calculated quantum chemical parameters for tested compounds

Compound	DFT/B3LYP/6-31G (d) and DFT/B3LYP/6-311G(d,p)			
	HMBI		TMBI	
E(ZPE)(eV)	-13443.4	-13447.1	-22228.5	-22232.1
E_{HOMO} (eV)	-5.832	-6.069	-5.628	-5.856
E_{LUMO} (eV)	-0.210256	-0.493408	-0.250512	-0.556240
$\Delta E = E_{LUMO} - E_{HOMO}$ (eV)	5.622	5.575	5.377	5.686
μ (Debye)	3.5447	3.6071	1.7225	1.7862
I(eV)	5.832	6.069	5.628	5.856
A(eV)	0.210256	0.493408	0.250512	0.556240
Mwt (g/mol)	148.06366	148.06366	164.04082	164.04082
χ	3.021	3.281	2.939	3.206
η	2.804	2.788	2.689	2.650
ΔN	0.349	0.305	0.379	0.335

In our case, we have ($E_{\text{HOMO}} = -5.628$ eV or $E_{\text{HOMO}} = -5.856$ eV) for TMBI whereas the values are ($E_{\text{HOMO}} = -5.832$ eV or $E_{\text{HOMO}} = -6.069$ eV) for HMBI. TMBI has also the weakest value concerning the gap ($\Delta E = 5.377$ eV or $\Delta E = 5.686$ eV).

From table VII, it is possible to observe that TMBI molecule has the lowest value of global hardness while the electronegativities calculated are almost similar for TMBI and HMBI. The fraction of electrons transferred is largest for TMBI as compared to that of HMBI. According to [31], low hardness value and high value of the fraction transferred enhances inhibition efficiency. Thus the higher inhibition effects of TMBI in comparison with HMBI may be attributed to the presence of S and N atoms at the same time in its molecular structure: the inhibition efficiency of organic compounds containing different donor atoms is in the sequence $S > N > O$ [32].

According to all these theoretical results we can see that it is possible to get better performance with TMBI. In order to verify these results, inhibition efficiencies were calculated using the following relation:

$$IE(\%) = \left(1 - \frac{W}{W_0}\right) * 100 \quad (11)$$

The experimentally found inhibition efficiencies of the studied molecules listed in table 8 allowed making some correlation between experimental values and the theoretical parameters from quantum chemical approach.

Table VIII: Inhibition efficiencies as a function of temperature for $C_{\text{inh}} = 10^{-3}$ M.

Temperature (°C)	IE (%) _{TMBI}	IE (%) _{HMBI}
25	88.7	85.3
35	91.0	86.1
45	91.7	87.3
55	92.0	89.8
65	92.6	90.2

Dipole moment indicates the hydrophobic character of the molecule [34]; low values of the dipole moment μ will favor the

accumulation of inhibitor molecules on the metallic surface.

In our case, the dipole moment of TMBI is lower than that of HMBI. It can be seen that TMBI has more inclination to get adsorbed on the metal surface than HMBI. Thus the inhibition efficiency of TMBI is higher than that of HMBI: theoretical results are in accordance with the experimental data to good extent.

On the other hand, the bonding tendencies of the inhibitors towards the metal atom can be discussed in terms of the HSAB (hard-soft-acid-base) [34,35] and the frontier controlled interaction concepts. General rule suggested by the principle of HSAB is that hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases. Besides, metal atoms are known as soft acids and hard molecules have a large HOMO-LUMO gap and soft molecules have a small HOMO-LUMO gap. In our case the HOMO-LUMO gap of TMBI is smaller than that of HMBI (Table VII). This result suggests that TMBI is softer base than HMBI. Hence, TMBI has a higher bonding tendency (greater adsorption and inhibition efficiency) towards the metal, atom Cu than HMBI.

Negative site in the electron donating molecule is usually the reactive center. In the studied molecules, the reactive centers are Oxygen, sulfur and nitrogen. Their atomic charges obtained through quantum calculations are presented in table IX.

Table IX: Atomic charges (with hydrogen summed into heavy atoms) of the compound.

Compound	¹² N	¹³ N	¹⁵ O	¹⁵ S	¹⁷ N	¹⁸ N
HMBI	-	-	-0.344	-	-0.533	-0.211
TMBI	-0.643	-0.301	-	-0.260	-	-

In table 9, the results derived from the application of an atomic population analysis are reported. The objective of this is to obtain a wider knowledge of the reactive properties of the systems of interest. For TMBI we can observe the

following excess negative charges (-0.643, -0.301, -0.260) on 12N, 13N and 15S respectively (Fig.4). For HMBI, the excess of negative charges are (-0.344, -0.533, -0.211) on 17N, 18N and 15O respectively (Fig.4). This means that TMBI has more excess charges than HMBI. Thus probably forming more stable Compounds or more protective films.

4. Conclusion

Both TMBI and HMBI are good inhibitors for copper in 1M HNO₃, generating inhibition efficiencies in order of 88.7% and 85.3% respectively at 10⁻³M.

The Langmuir adsorption isotherm was found to be closed to the adsorptive behavior of the studied compounds.

The negative values of the free adsorption enthalpy ΔG_{ad}^0 indicate a spontaneous adsorption process at all studied temperatures suggesting physisorption at low temperatures and chemisorption at high temperatures.

The comparison of the activated parameters of the free and the inhibited systems indicates that the corrosion process is enthalpy-controlled.

The values of the activation entropies $\Delta S^\ddagger$ show a decrease in disordering when the reactants are transforming into activated complex.

Theoretical results obtained from quantum calculations using Gaussian 03 W suite of programs are in accordance with the experimental data to good extend.

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