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# Amino acids as corrosion inhibitors for copper in nitric acid medium: Experimental and theoretical study

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## Abstract

The corrosion inhibition of copper in 1 M $HNO_3$ was studied by gravimetric and potentiodynamic polarization by use of amino acids such as : Acid aspartic (Asp), Acid Glutamic (Glu), Alanine (Ala), Asparagine (Asn), Glutamine (Gln), Leucine (Leu), Methionine (Met), and Threonine (The). The results obtained the from two different techniques are comparable, and show that Met is the best inhibitor for the corrosion of copper in 1M $HNO_3$. Correlation between inhibition efficiency and quantum chemical calculations using semi empirical (AM1 and MNDO) and ab-initio methods is discussed.

*Keywords:* Corrosion, inhibition, copper, amino-acids, nitric acid.

## Introduction

Copper and its alloys are very widely used materials for their excellent electrical and thermal conductivities in many applications such as electronics and in the manufacture of integrated circuits. Copper is a relatively noble metal, requiring strong oxidants for its corrosion or dissolution. The chemical dissolution and electrolytic plating are the main processes used in the fabrication of electronic devices. The most widely used corrosive solution contains nitric acid, so this medium has induced a great deal of research on copper corrosion [1]. One of the most important methods in the corrosion protection of copper is the use of organic inhibitors.

Survey of literature shows that organic compound and their derivatives such as azoles [2-8] amines [9-11], amino acids [12-17], containing sulfur [18], and many others showed inhibition effect for the corrosion of copper and copper alloys in different media. It is noticed that presence of heteroatoms such as nitrogen, sulphur, oxygen and phosphorous in the organic compound molecule improves its action as copper corrosion inhibitor. This is explained by the presence of vacant d orbitals in copper atom that form coordinative bonds with atoms able to donate electrons. Unfortunately, most of these compounds are synthetic chemicals which may be very expensive, toxic and hazardous to living creatures and environment e.g. benzotriazole (BTAH) [19] and its derivatives are excellent corrosion inhibitors for Cu and its alloys but these are toxic [20, 21].

To avoid the toxicity of numerous compounds tested as inhibitors [15, 22- 24], natural compounds, regarded as environmentally friendly, have also been studied [22-25]. Amino acids have been tested as inhibitors of corrosion of a variety of metals, for example copper, lead, aluminium, and steel corrosion in acidic media [14, 26-35]. They are relatively easy to produce with high purity at low cost, non-toxic, and are soluble in aqueous media. Methionine derivatives are sulphur-containing amino acids. Methionine itself is investigated as possible corrosion inhibitor for mild steel [31, 36–39], for low carbon steel [33] and copper [1]. Ashassi-Sorkhabi and al. [29] reported the successful application of methionine as a corrosion inhibitor for aluminium in mixed acid solution and pointed out the role of S atom in increasing the interaction of the molecule with the metal surface. The same results have been reported by K.F. Khaled in their study of the influence of some selected sulphur-containing amino acids, namely L-methionine (MIT), L-methionine sulphoxide (MITO) and L methionine sulfone (MITO2), on the inhibition of copper corrosion in 1.0 M $HNO_3$ solutions [1].

The aim of the present work is to investigate the effect of some amino acids such as alanine, leucine, asparagines, acid aspartic, glutamine, acid glutamic, threonine and metionine, on the corrosion behavior of copper in nitric acid solution, by use of electrochemical polarization measurements and weight-loss measurements. Theoretical calculations provide an explanation of the differences among these inhibitors. Among quantum chemical data calculated, the energies of the HOMO and LUMO, and the difference between these ($\Delta E = E_{LUMO} - E_{HOMO}$) are discussed.

## Materials and methods

The working electrode used in this work is made from copper of 99% purity. The electrode was provided in disc form and was embedded in epoxy resin in a Teflon holder with electrical contact being achieved by means of a copper wire threaded into the base of the metal sample. The aggressive solution, 1 $molL^{-1}$ $HNO_3$, was prepared by dilution of analytical- grade 65% nitric acid with bidistilled water. The amino acids (Asp, Asn, Glu, Gln, Leu, The and Met) tested as inhibitors were the commercial products (> 99 % purity). Their molecular structures are shown in Fig. 1.

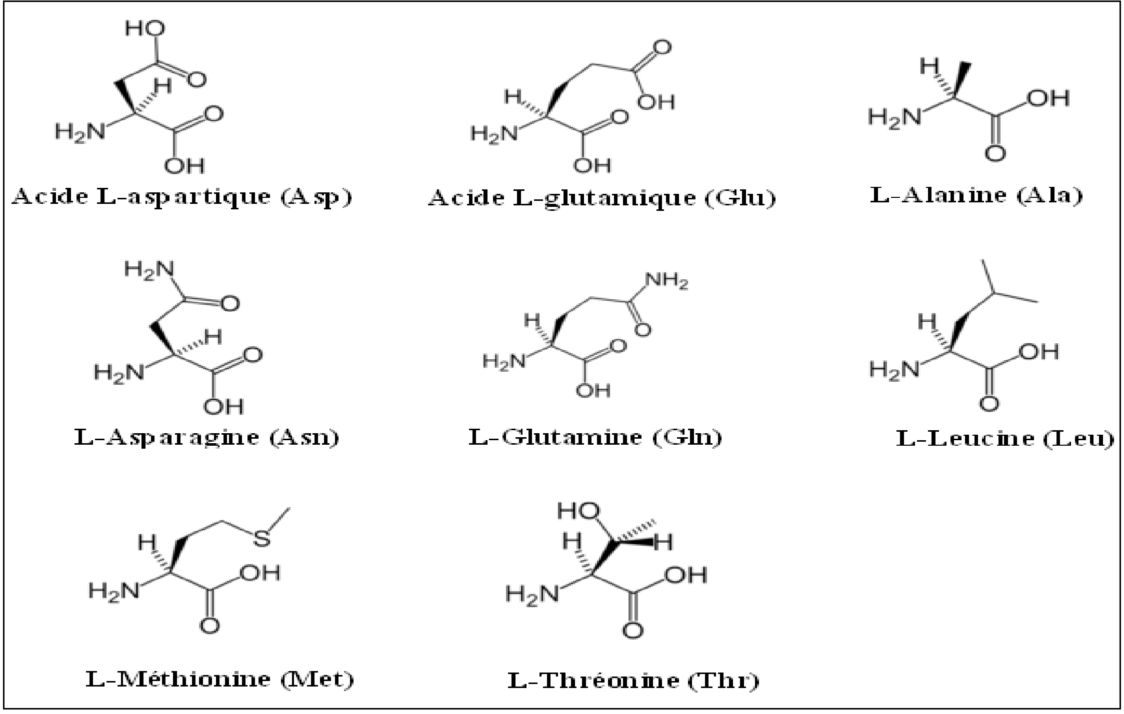


**Figure 1:** Molecular structure of amino acids tested.

Before the measurements, the copper specimens were polished successively with emery paper up to 1000 grade, then rinsed thoroughly with acetone and bidistilled water. Potentiodynamic polarization curves were recorded by use of a PGP 201 potentiostat combined with "Volta Master 1", the scan rate was 60mV/min. The potential ranged from –800 to +500 mV/SCE. Electrochemical measurements were performed with a conventional three-electrode electrochemical cell (with thermostat) consisting of platinum electrode as auxiliary electrode, a saturated calomel electrode (SCE) as reference, and Cu metal as working electrode. The Cu electrode was a disc of pure copper of surface area 0.35 $cm^2$; before measurements it was maintained at its free potential of corrosion for 30 min. All experiments were carried out in freshly prepared solution at constant temperature, 20 ± 0.1 °C using a thermostat.

Gravimetric methods were conducted on copper test samples of a total surface area 12$cm^2$. All experiments were carried out under total immersion in 75 mL test solution. Mass loss was recorded by use of an analytical balance. Three measurements were performed in each case and the mean value of the weight loss has been reported.

Computation of the energies of the molecules, $E_{HOMO}$, $E_{LUMO}$, energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), and charges density of the heteroatoms, was been performed by use of AM1 (Austin Model 1) [40] and MNDO (Modified Neglect of Differential Overlap) [41], semi-empirical methods implemented in MOPAC 6.0 software [42], and ab-initio methods. Complete geometrical optimization of the investigated molecules are performed by use of DFT (density functional theory) with the Beck's three-parameter exchange functional and the Lee–Yang–Parr nonlocal correlation functional (B3LYP) with the 6-31G* basis set, as implemented in the Gaussian 03 software package [43].

## 3. Results and discussion

### *3.1. Polarisation measurements*

Fig. 2 collects the cathodic and anodic curves of copper in deaerated acid in the absence and presence of amino acids studied at $10^{-3}$ M at 20°C. Cathodic polarization curves gave rise to parallel Tafel lines, indicating that the hydrogen evolution reaction is activation controlled and the presence of various amino acids tested does not affect the mechanism of this process. The same results have been reported by other authors [44, 45]. Table 1 gives values of corrosion potential ($E_{corr}$), current

($I_{corr}$) calculated by extrapolation of the linear parts of the cathodic Tafel lines to $E_{corr}$, cathodic Tafel slope ($b_c$) for amino acids compounds at the concentration of $10^{-3}$ M in 1mol/L $HNO_3$. In the case of polarization method, the inhibition efficiency (E%) is calculated according the following relation:

$$E_I(\%) = \left(1 - \frac{I'_{corr}}{I_{corr}}\right) \times 100$$

Where $I_{corr}$ and $I'_{corr}$ are the uninhibited and inhibited corrosion current densities respectively.

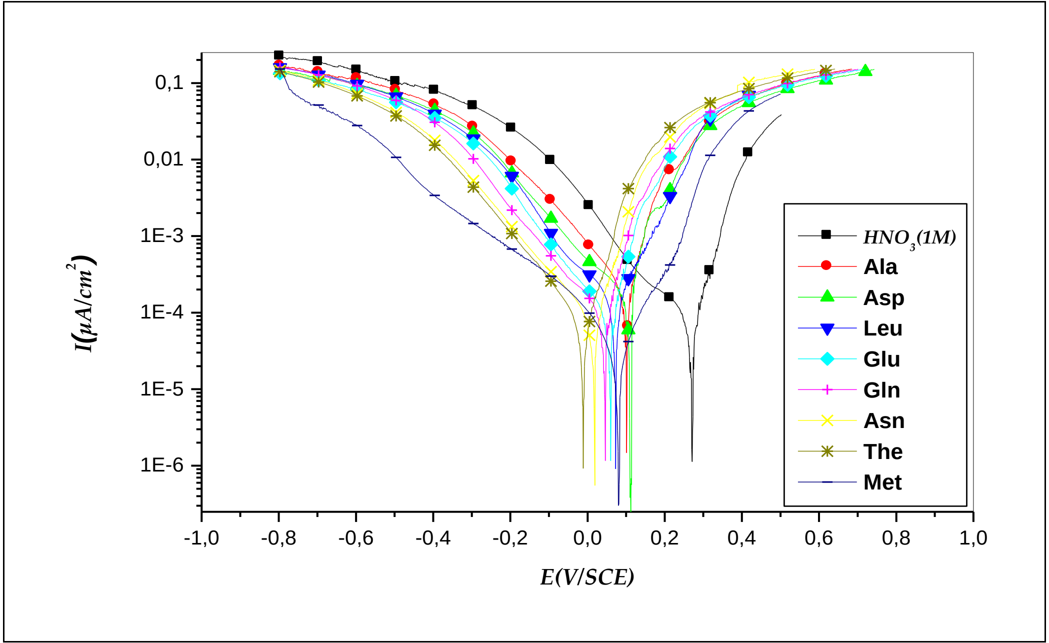


**Figure 2:** Polarization curves for copper in 1 mol $L^{-1}$ $HNO_3$ solutions in the absence and presence of amino acids at $10^{-3}$M.

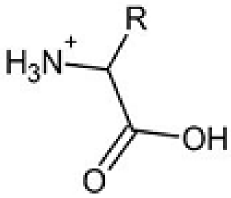
From Table 1, it was clearly seen that the presence of amino acids compounds at $10^{-3}$ M reduces the corrosion rate of copper in nitric acid solution. The current density of the cathodic curves is lower in the presence of Met than in the presence of other inhibitors. This indicates that Met is good inhibitor of corrosion in 1mol/L $HNO_3$ solution, and the inhibitive action of the amino acids under examination decreases in the order: **Ala <Asp <Leu <Glu <Gln <Asn <The <Met.**

This order is mainly due to the nature of the radical R in the molecular structure. It's well known that different substituants on the organic molecule polarize the functional group in a different manner [44]. This indicates that the protective effect of Met is not solely due to their reactivity with the nitric acid.

In acidic media, $NH_2$ of amino acid molecule is readily protonated to form $NH_3^+$. Also the addition of Ala and Leu leads to low E%. This phenomenon is essentially due the presence of aliphatic radical R of Ala and Leu. But when the radical contains heteroatom as N, O or S a decrease of corrosion current densities in the presence of Met, The, Glu, Gln, Asp and Asn at $10^{-3}$ M was noted. $E_{corr}$ shifts to more negative values in the presence of amino acids tested.

**Table 1:** Electrochemical data from the potentiodynamic curves obtained for pure copper at 20°C in 1mol $L^{-1}$ $HNO_3$ in the presence of the different amino acids tested.

| Solution | $E_{corr}$ (mV/SCE) | $I_{corr}$ ($\mu A/cm^2$) | bc (mV/dec.) | $E_I$ (%) |
|---|---|---|---|---|
| **$HNO_3$ (1M)** | 261.00 | 84.07 | -162.78 | --- |
| **Ala** | 110.93 | 63.46 | -154.07 | 24.51 |
| **Asp** | 119.57 | 60.47 | -164.54 | 28.07 |
| **Leu** | 81.10 | 55.62 | -168.47 | 33.84 |
| **Glu** | 68.13 | 52.50 | -171.23 | 37.55 |
| **Gln** | 50.10 | 50.27 | -173.47 | 40.20 |
| **Asn** | 25.33 | 46.23 | -163.03 | 45.01 |
| **The** | 4.12 | 41.69 | -173.35 | 50.41 |
| **Met** | 88.55 | 16.49 | -228.79 | 80.38 |



The inhibition efficiency obtained from polarization method is close to those deduced from gravimetric method.

It is observed that, the corrosion potential $E_{corr}$ shifted to more negative values of the amino acids tested. This result indicates that the inhibitors have been adsorbed to cathodic areas. This remark is justified also by the diminution of cathodic current densities. The same results have been reported by other authors [34, 22].

Then, the addition of amino acids molecules in nitric acid solution seems that no effect on anodic behaviour is observed. This result shows that the inhibitory action of these compounds depends on the potential for higher Ecorr potential inhibitory character disappears.

The electrochemical cathodic and anodic reactions of copper in deaerated $HNO_3$ solution can be described as follows [45]:

Anodic reaction:

$$\mathbf{Cu \longrightarrow Cu^{2+} + 2e^-} \qquad \mathbf{(1)}$$

Cathodic reactions:

$$\mathbf{NO_3^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O} \qquad \mathbf{(2)}$$

$$\mathbf{NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O} \qquad \mathbf{(3)}$$

$$\mathbf{2H^+ + 2e^- \longrightarrow H_2} \qquad \mathbf{(4)}$$

### *3.2. Gravimetric method*

The effect of addition of the amino acids at a concentration of $10^{-3}$ mol $L^{-1}$ on the corrosion of copper in 1M $HNO_3$ solutions was studied by measurement of weight loss at 20°C after immersion for 4h (Fig. 3). The values of the corrosion rate ($V_{corr}$) and inhibition efficiency are listed in Table 2. The inhibition efficiency ($E_G$) was determined by use of the relationship:

$$E_G\,(\%) = \frac{V_{corr} - V'_{corr}}{V_{corr}} x100$$

where $V'_{corr}$ and $V_{corr}$ are the rate of corrosion of copper with and without the inhibitor, respectively.

Gravimetric measurements show the rate of corrosion is lower in the presence of Met than in the presence of other inhibitors. Met is very efficient inhibitor of corrosion of copper in the acid solution, with maximum inhibition efficiency of 93.98% at $10^{-3}$M.

The essential effect of corrosion inhibition is because of the presence of electron donor groups (S, N, O) in the molecular structure of the Met. It is well known that the presence of heteroatoms, for nitrogen, oxygen, sulfur and phosphorus, in the inhibitor structure results in better inhibition [15, 23, 28, 46]. Also the most organic substance employed as corrosion inhibitors can adsorb on the metal surface through heteroatoms. Its inhibition efficiency should follows the sequence $O < N < S < P$ [44, 46]. Electron pairs on the heteroatoms can be shared with metal orbitals, forming an insoluble complex that protects the surface from the aggressive ions by blocking of its corrosion sites and hence decreasing the corrosion rate. [4]. The presence of pairs of free electrons on soufre, nitrogen and oxygen atoms favours adsorption of Met and, thus, the best efficiency of these inhibitor [1, 15, 26]. This processes facilitated by the presence of d vacant orbitals of low energy in the copper ions, as observed in transition group metals.

**Table 2** : Electrochemical data from the potentiodynamic curves obtained for pure copper at 20°C in 1mol $L^{-1}$ $HNO^3$ in the presence of the different amino acids tested

| **Solution** | **$V_{corr}$ (mg/h.cm$^2$)** | **$E_G$ (%)** |
|---|---|---|
| **$HNO_3$ (1M)** | 0,054 | - |
| **Ala** | 0.044 | 18.56 |
| **Leu** | 0.035 | 35.18 |
| **Gln** | 0.032 | 40.74 |
| **Glu** | 0.034 | 37.04 |
| **Asn** | 0.031 | 42.59 |
| **Asp** | 0.037 | 31.48 |
| **The** | 0.028 | 48.15 |
| **Met** | $3.250.10^{-3}$ | 93.98 |

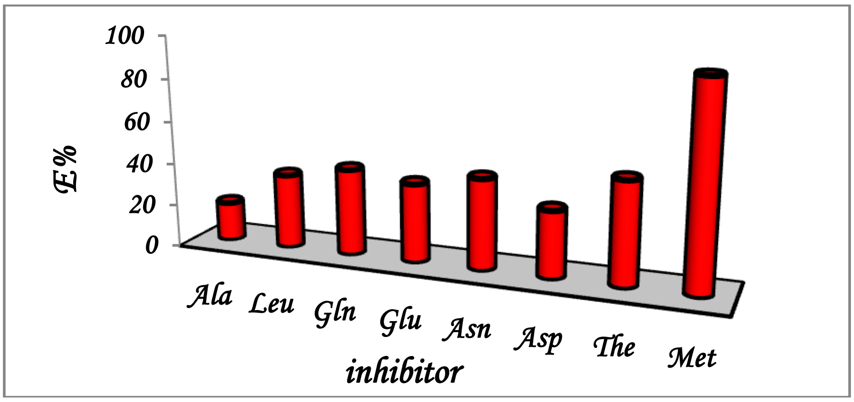


**Figure 3:** Variation of the efficiency of inhibition of corrosion of copper in 1M $HNO_3$ by amino acids at $10^{-3}$M.

Recently it was found that the formation of donor–acceptor surface complexes between free electrons of an inhibitor and a vacant d orbital of a metal is responsible for the inhibition of the corrosion process [47, 1]. Also, the best E% can be attributed to the presence of group –S-$CH_3$. This group is more a donor of electron and it offers itself the possibility to be a center of adsorption beside the atom of nitrogen [48, 46]. In the case of The, oxygen atom in aliphatic chain increases the interaction of molecule with metal surface. Although Asp, Asn, Glu and Gln has a radical R which contains nitrogen and oxygen, effectiveness remains low because the existence of –CO groups at atoms [35, 46].

### *3.3. Quantum chemical studies*

#### *3.3.1. Semi-empirical methods*

In order to obtain more information about the molecular energy and the inhibitory action of this amino acid, semi-empirical quantum theoretical calculations were performed using the AM1 and MNDO methods. Because the amino acids tested are present in the protonated forms in 1 mol $L^{-1}$ $HNO_3$ solution, the protonated forms of these amino acids were used for quantum chemical calculations. The values of energy of the highest occupied molecular orbital ($E_{HOMO}$), the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), and the gap ($\Delta E = E_{LUMO} - E_{HOMO}$) between $E_{HOMO}$ and $E_{LUMO}$ are listed in table 3.

**Table 3:** Quantum chemical data for the protonated forms of amino acids tested calculated by use of the AM1 and MNDO semi-empirical methods.

| Composés | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | ΔE (eV) |
|---|---|---|---|
| **AM1** | | | |
| **Ala** | -16.20 | -4.80 | 11,40 |
| **Asp** | -15.81 | -4.69 | 11,11 |
| **Leu** | -15.25 | -4.46 | 10.79 |
| **Glu** | -15.07 | -4.49 | 10.57 |
| **Gln** | -14.68 | -4.30 | 10.38 |
| **Asn** | -14.63 | -4.66 | 10.08 |
| **The** | -14.05 | -4.51 | 9.55 |
| **Met** | -12.06 | -3.98 | 8.07 |
| **MNDO** | | | |
| **Ala** | -16.03 | -4.98 | 11.05 |
| **Asp** | -15.55 | -4.94 | 10.61 |
| **Leu** | -15.87 | -4.73 | 10.40 |
| **Glu** | -14.68 | -4.44 | 10.24 |
| **Gln** | -14.89 | -4.78 | 10.11 |
| **Asn** | -15.02 | -5.11 | 9.91 |
| **The** | -14.20 | -4.67 | 9.54 |
| **Met** | -13.02 | -4.98 | 8.03 |

HOMO energy is often associated with the electron donating ability of a molecule. The less negative HOMO energy and the smaller energy gap ΔE are often interpreted by a stronger chemisorption bond and perhaps greater inhibition efficiency [44, 49]. Figure 4 shows linear plots of ΔE against inhibition efficiency of the amino acids; correlation coefficients were R = 0.991 and R = 0.995, respectively, by the AM1 and MNDO methods.

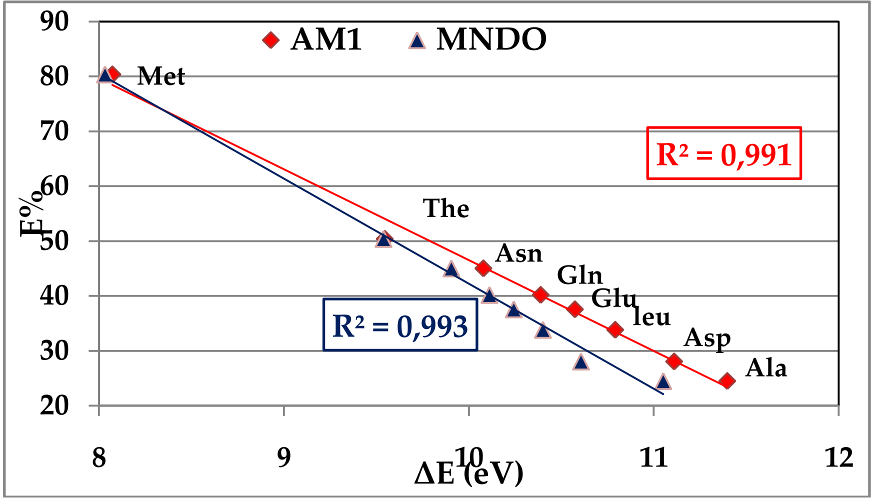


**Figure 4:** Correlation between energy gaps ($\Delta E = E_{LUMO} - E_{HOMO}$) and efficiency of inhibition corrosion by the amino acids tested.

Examination of Table 3 reveals that ΔE obtained by this method decreases in the order: **Ala < Asp < Leu < Glu < Gln < Asn < Thre < Met**. This result indicates that electron transfer between the HOMO and LUMO is facilitated by Met, for which inhibition efficiency is maximum. The smaller energy gap (ΔE) obtained for Met can be interpreted on the basis of stronger adsorption [7, 45, 46]. The stability of the Cu-Met complexes depends, essentially, on the differences between the interacting orbital energies [46]. These jumps may be explained by the calculation of the net atomic charges and electron density [44, 50].

The optimum conformations of the protonated forms of Met, Thre, Asn, Asp, Gln, Glu, Leu and Ala are shown in Fig. 5. The net charge on the heteroatoms of these amino acids is listed in Table 4. Comparison of the calculated values shows that on the atomic charge is always more negative on the oxygen atom than on the nitrogen atom for the compounds investigated except Gln and Asn. The net charge of sulphur atom being 0.103 e, is adsorbed on the surface of metal. Furthermore, the electron density on the oxygen atom is higher for Met and the electron density of sulphur atom being 5.90 (Table 5), is adsorbed on the surface of metal. The presence of both -OH and –S-$CH_3$ groups in Met leads to synergistic intramolecular effect [44, 51]. These properties enhance the possibility of Met adsorbed more strongly by the copper surface than other amino acids, which explains why the efficiency of inhibition obtained with Met is higher. From these results the comparative study, it’s evident that Met is the excellent corrosion inhibitor for copper in nitric acid medium.

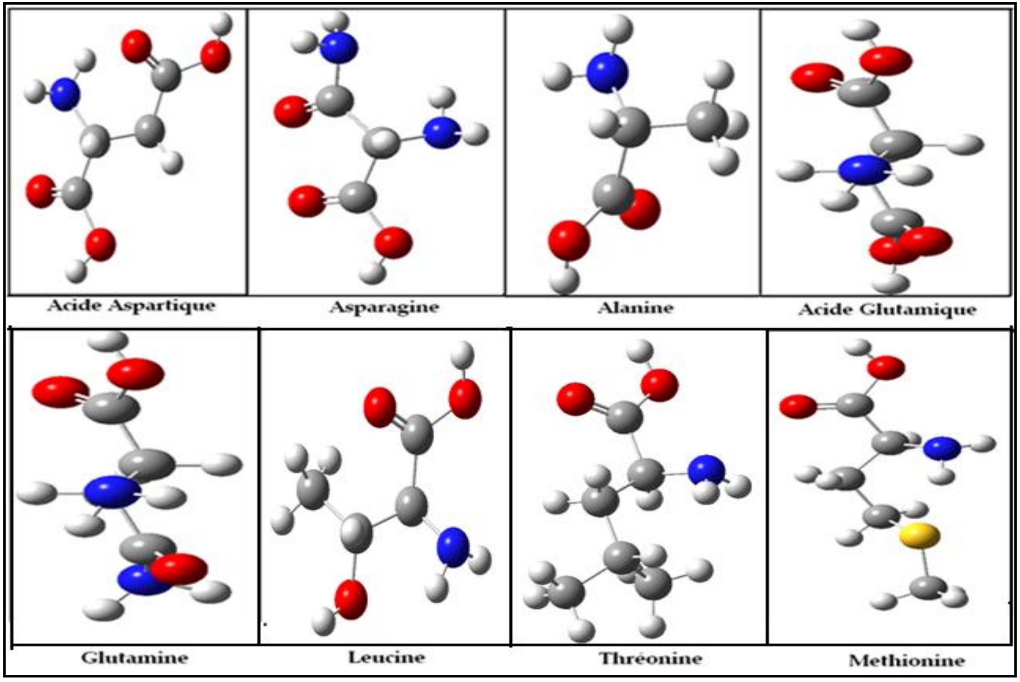


**Figure 5:** The optimum conformations of the forms of Met, Thre, Asn, Asp, Gln, Glu, Leu and Ala.

**Table 4:** Net atomic charges of amino acids compounds calculated by the AM1 method.

| **inhibitor** | **$O_3$** | **$O_4$** | **$O_8$** | **$O_{14}$** | **$O_{15}$** | **$O_{16}$** | **$O_{17}$** | **$N_5$** | **$N_{16}$** | **$S_{14}$** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Ala** | -0.322 | -0.263 | - | - | - | - | - | -0.067 | - | - |
| **Asp** | -0.253 | -0.330 | - | -0.336 | -0.218 | - | - | -0.067 | - | - |
| **Leu** | -0.251 | -0.342 | - | - | - | - | - | -0.064 | - | - |
| **Glu** | -0.241 | -0.340 | - | - | - | -0.328 | -0.292 | -0.065 | - | - |
| **Gln** | -0.241 | -0.344 | - | - | - | -0.355 | - | -0.065 | -0.413 | - |
| **Asn** | -0.319 | -0.272 | - | -0.133 | - | - | - | -0.067 | -0.418 | - |
| **The** | -0.318 | -0.268 | -0.360 | - | - | - | - | -0.060 | - | - |
| **Met** | -0.322 | -0.271 | - | - | - | - | - | -0.116 | - | 0.103 |

**Table 5:** Density electronic on the heteroatoms of the amino acids, obtained by the AM1 method.

| | **Density** | **Electronic** | **On Heteroatom** |
|---|---|---|---|
| **Molécule** | $O_4$ | $N_5$ | S |
| **Met** | 6.27 | 5.12 | 5.90 |

## Conclusion

In this work, amino acids such: Ala, Leu, Asp, Asn, Glu, Gln, Thre and Met, where tested as inhibitors of corrosion of copper in 1 mol $L^{-1}$ $HNO_3$ solutions. For this purpose electrochemical polarization measurement, weight-loss measurements, and theoretical calculations were used. The results are in good agreement and the main conclusions are as follows:

- All the amino acids investigated inhibited corrosion of copper in 1 mol $L^{-1}$ $HNO_3$.
- The efficiency of inhibition of corrosion by the amino acids depends on their molecular structure. It increases in the order: **Ala < Asp < Leu < Glu < Gln < Asn < Thre < Met.**
- Met is the best inhibitor of corrosion of copper.
- Corrosion inhibition can be attributed to adsorption of the molecules by interaction of the copper with nitrogen, oxygen and sulphur atoms; this forms a barrier blocking corrosion of the copper.
- Results obtained from electrochemical studies and weight loss measurements were in good agreement.
- By use the quantum chemical approach it may be possible to predict molecular structures resulting in better inhibition of corrosion.

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