# Theoretical Study on the Structural Effect of Sulfur Containing Amino Acids As Corrosion Inhibitors On Brass In HClO$_4$

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**Abstract:** Quantum chemical calculations have been employed for the inhibition efficiency on Sulphur containing amino acids, Methionine (METH), cysteine (CYSH) and cystine (CYS) for brass in HClO$_4$ by means of density functional theory (DFT) methods B3LYP/6-31G*, RHF/6-31G* and semi-empirical method (AM1) in gas phase, The calculated quantum chemical parameters correlated to the inhibition efficiency are, E$_{HOMO}$, E$_{LUMO}$, energy of the gap ($\Delta$E), charge on the reactive center, dipole moments and global hardness. The order of inhibition efficiencies as follows: METH> CYSH> CYS.

## 1. Introduction

Amino acids complex with metals [1-6] like Zn, Cu, Co, Fe, Cr and find widespread use as corrosion inhibitors because they are nontoxic [7]. These are ampholytes having an isoelectric pH of ~ 5.50 and hence exist as cations in acidic medium [8,9]. These compounds with groups containing lone pair of electrons act as good inhibitors for corrosion of metals like Cu [10] and brass [11]. In addition, the presence of halide ions along with the inhibitors has been found to improve their inhibitor efficiency [12].

The inhibition efficiency of amino acids, glycine, L(-)aspartic acid and L(-) glutamic acid and their corresponding benzene sulphonyl derivatives on brass in aqueous sodium chloride solution have been studied using potentiodynamic polarization electrochemical impedance spectroscopy [13]. Some work has been done on the inhibition effect of some amino acids on copper corrosion in acidic chloride solutions [14].The action of four amino acids containing sulfur on the corrosion of mild steel in phosphoric acid solution with and without Cl$^-$, F$^-$ and Fe$^{3+}$ ions near and at the corrosion potential ($E_{corr}$) was reported [15], using both the polarization resistance method and electrochemical impedance spectroscopy (EIS). Both cysteine and *N*-acetylcysteine (ACC) showed higher inhibition efficiency than methionine and cystine [15]. Inhibition effect of cysteine (Cys) and glycine (Gly) towards the corrosion of Cu10Ni alloy in sulfide polluted NaCl solution was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques [16]. It was found that these investigated compounds act as good

inhibitors for the corrosion of Cu10Ni alloy in polluted NaCl solutions [16]. The addition of KI was found to have a synergistic effect which enhanced the inhibition efficiency [16].

Experimental means are useful in explaining the inhibition mechanism but they are often expensive and time consuming. Advance in computer hardware and software and in theoretical chemistry have brought high-performance computing and graphical tools within the reach of many academic and industrial laboratories. Recently more corrosion publications contain substantial quantum chemical calculations [17]. Such calculations are usually used to explore the electronic properties of the inhibitors, the effect of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, the difference between highest occupied molecular orbital and lowest unoccupied molecular orbital energies (E$_{LUMO}$-E$_{HOMO}$), charge on the reactive center, dipole moments, global hardness and total energies had to be investigated to achieve the appropriate correlation [18, 19].

The inhibitor efficiency (%P) was calculated experimentally of three amino acids, Methionine (METH), cysteine (CYSH) and cystine (CYS) using weight loss, Tafel extrapolation and electrochemical impedance spectroscopy (EIS) method. Results obtained showed that methionine ,(METH) has the highest inhibition efficiency, while cystine (CYS) has the least inhibition efficiency for brass in 0.1M HClO$_4$ [20].

The aim of this work is to extend these investigations in order to discuss the relationship between quantum

chemical calculations and experimental inhibition efficiencies of these amino acids by Am1, RHF/6-31G* and B3LYP/6-31G* from these data, by determining quantum chemical parameters such as the energies of the highest occupied molecular orbital ($E_{HOMO}$) and the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), the energy difference ($\Delta E$) between $E_{HOMO}$ and $E_{LUMO}$, charge on the reactive center , dipole moments and global hardness.

## 2. Method of calculations

Firstly theoretical calculations were carried out by using AM1 semi-empirical methods in MOPAC2007 program, implemented on an Intel Pentum (R) 1.86 GB personal computer. Initial estimates for the geometries of all the structures were obtained by molecular mechanics program (ACD11) for Widows, followed by full optimization of all geometrical variables (bond lengths, bond angles and dihedral angles), without any symmetry constraint, using AM1 semi-empirical methods in gas phase. The structures obtained from AM1 calculations were fully re-optimized by using Restricted Hartree Fock (RHF) and Density functional theory (DFT) methods to estimate the quantum chemical parameters. Calculations at the RHF and DFT level were performed with basic sets 6-31+g(d) and 6-31G* respectively. For this purpose the Gaussian 03 Quantum Chemistry Program with complete geometry optimization was used.

## 3. Results and Discussion

The chemical structures of the compounds under investigation are presented in figure 1. The optimized molecular structures of the studied molecules using B3LYP/6-31G* methods are shown in figure 2.
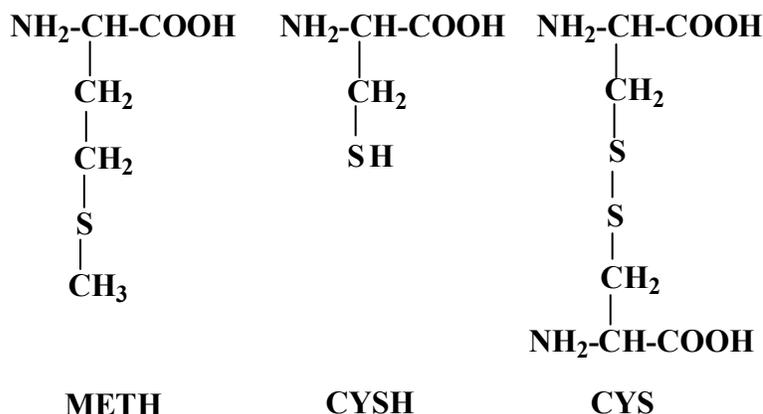


**Figure 1. The structure of amino acids**

The calculated quantum chemical indices $E_{HOMO}$, $E_{LUMO}$, $E_L$-$E_H$, global hardness, total energies, dipole moment and inhibition efficiencies obtained from the experimental measurements are given in table 1, Mulliken atomic charges on nitrogen, oxygen, sulphur and carbon atoms are shown in table 2. It has been proven that local electron densities or charges are important, in many chemical reactions and physicochemical properties of compounds [21]. Inhibition action of organic molecules can be explained by the adsorption on metal surface. Since the surface of the brass is positively charged in acidic solution [22], table 2 show that all nitrogen, oxygen and carbon atoms bonded to the sulphur of amino acids carry the negative charges, this indicate that these atoms are the negative charge centers which could offer electrons to the brass surface to form a coordination type of bond.

Another important point to be considered in the energy level terms is gap between the HOMO and LUMO energies for the studies molecules (1-3).

Cherry *et al.*[23] have used the concept of LUMO-HOMO energy gap in developing theoretical models which **is** capable of explaining the structure and conformation barriers in many molecular systems qualitatively. Low absolute values of the energy band gap ($\Delta E$) gives good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low [17]. According to the data in table 1, there is a good correlation in LUMO-HOMO energy gap by these methods in gas phase, it can be seen that Methionine (METH) is best inhibitor and has smallest LUMO- HOMO gap i.e (9.363 eV), (11.195 eV) and (6.301 eV) by AM1, RHF/ 6-31+g(d) and B3LYP/6-31G* respectively, but the cystine (CYS), which is least inhibitor and has highest LUMO-HOMO gap i.e (11.717 eV), (11.839 eV) and (7.161 eV) by AM1, RHF/ 6-31G* and B3LYP/6-31G* respectively. Thus the difference between the LUMO- HOMO of the METH and LUMO- HOMO of CYS by B3LYP/6-31G* method is of 0.860 eV caused an inhibition increase to 21.0%.

As can be seen from table 1 for all methods of calculations, the inhibition effiencies increases as the $E_L$-$E_H$ values decrease, which indicates the stability of formed complexes between the amino acids and brass in perchloric acid media, i.e the order of inhibition efficiencies as follows: METH> CYSH> CYS.as can be obtained from experimental data [20]. This indicates that the best correlations between experimental and calculated inhibition effiencies were obtained by using AM1, RHF/ 6-31+g(d) and B3LYP/6-31G* in gas phase for amino acids, correlations are almost in the same order. Correlation coefficients greater than 60% were well accepted in quantum chemical calculations of corrosion studies [24].

   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, low LUMO energy indicates the ability of the molecules to accept electrons [17]. The results obtained by AM1 and RHF/ 6-31+g(d) method in gas phase, (table 1) show that METH has highest HOMO energy ($E_{HOMO}$= -8.889, -9.526 eV) among these inhibitors. Whereas the CYS has low HOMO energy ($E_{HOMO}$=-9.599, -10.281). Figure 3 shows the shapes of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the compounds under investigations. From these figures it can be concluded that the compounds adsorbed on the mild brass surface by using the amino acids moiety which contains the heteroatom nitrogen, oxygen and sulphur.

   The higher inhibitor efficiency of METH as compared to CYSH may therefore be attributed to the presence of $CH_3$ in the former which facilitates a stronger interaction of inhibitor with the surface through its induction effect, results in a great increase of HOMO energy level (and a decrease of energy of the gap $E_{LUMO}$- $E_{HOMO}$) obviously. The lower inhibitor efficiency of CYS compared to CYSH may be attributed to the S-S link in the former which may is believed to adsorb on brass *via* cleavage of the S–S bond and formation of adsorbed thiol radicals 2RS [25] and so adsorption of cystine on brass will form a film equivalent to that formed by the corresponding a dialkyl disulfide [25]. In the measurements of cystine surface coverage, we assumed that the adsorption of cystine follows the formation of radical which reduce the electronegativity of each 'S' atom and lowering $E_{HOMO}$ value of CYS molecule. In addition, the bulky molecule is sterically not conducive for stronger interaction of the inhibitor with the surface.
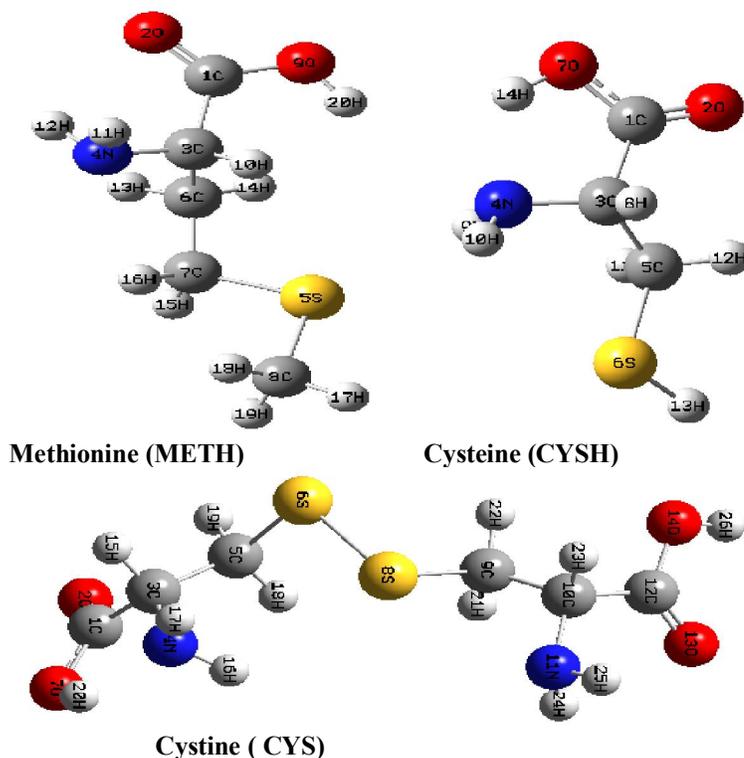


**Methionine (METH)**          **Cysteine (CYSH)**

**Cystine ( CYS)**
**Figure 2. The optimized structure of Amino acids by B3LYP/6-31G***

**Table 1. AM1, RHF/6-31+g(d)and B3LYP/6-31G\* data for amino acids (1-3)**

| Inhibitor | $E_{LUMO}$ (eV) | $E_{HOMO}$ (eV) | $E_L$-$E_H$ (eV) | Hardness eV | Dipole Moment (D) | Total energy eV | % Inhibition in 0.1M $HClO_4$ |
|---|---|---|---|---|---|---|---|
| AM1 | | | | | | | |
| 1 METH | 0.474 | -8.889 | 9.363 | 4.681 | 3.979 | -1835.1 | 71.0 |
| 2 CYSH | 0.234 | -9.458 | 9.692 | 4.846 | 3.217 | -1523.5 | 65.0 |
| 3 CYS | 2.118 | -9.599 | 11.717 | 3.740 | 3.557 | -3019.7 | 50.0 |
| | | | | | | | |
| RHF/6-31+g(d) | | | | | | | |
| 1 METH | 1.669 | -9.526 | 11.195 | 5.5975 | 4.235 | -21699.699 | 71.0 |
| 2 CYSH | 1.659 | -10.158 | 11.817 | 5.9085 | 4.011 | -19575.453 | 65.0 |
| 3 CYS | 1.557 | -10.281 | 11.839 | 5.9195 | 5.205 | -39256.923 | 50.0 |
| | | | | | | | |
| $B_3LYP$/6-31G\* | | | | | | | |
| 1 METH | -6.157 | 0.144 | 6.301 | 3.1505 | 3.444 | -21784.047 | 71.0 |
| 2 CYSH | -6.880 | -0.064 | 6.816 | 3.408 | 3.772 | -19644.652 | 65.0 |
| 3 CYS | -7.029 | 0.132 | 7.161 | 3.5805 | 5.303 | -19627.334 | 50.0 |

% inhibition efficiencies are taken from reference [20]

**Table 2. Mulliken atomic charges of amino acids (1-3) by B3LYP/6-31G\***

| Molecule | C1 | O2 | C3 | N4 | S5 | C5 | S6 | C6 | C7 | O7 | C8 | O9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 METH | 0.582 | -0.445 | 0.053 | -0.075 | 0.057 | - | - | 0.040 | -0.032 | - | -0.032 | -0.147 |
| 2 SYSH | 0.613 | -0.460 | 0.098 | -0.097 | - | -0.016 | 0.004 | - | - | -0.141 | | |
| 3 CYS | 0.622 | -0.463 | 0.097 | -0.102 | 0.018 | - | - | - | -0.032 | -0.140 | | |

Another property calculated for these molecules is the global hardness η, calculated as ΔE/2, which is parameter that gives important information about the reactive behavior of the molecule, and can be defined under the principle of chemical hardness and softness (HSAB), [26], as can be seen in table 1, the METH exhibits the minimum hardness value, whereas the CYS presents the maximum value of hardness this indicate that METH is potential corrosion inhibitor over the other.

The dipole moment is another way to obtain data on the electronic distribution in a molecule and is one of the properties more used traditionally to discuss and to rationalize the structure and reactivity of many chemical systems [27], according to results in table 1, METH has low value of dipole moment (3.444 D) and CYS has high value of diploe moment (5.303 D) by B3LYP/6-31G\* methods, which explain the higher inhibition efficiency of METH than the other two inhibitors, i.e. the order of inhibition efficiencies as before: METH > CYSH > CYS.

**4. Conclusions**

Through AM1 semi-empirical, RHF/6-31+g(d) and B3LYP/6-31G\* quantum chemical calculations a correlation between parameters related to structure of some Sulphur containing amino acids and their ability to inhibit the corrosion process could be established.

The inhibition efficiency of sulphur containing amino acids obtained experimentally increase with the increased in $E_{HOMO}$, and decreased in $E_{LUMO}$ and decreased in the energy of the gap (ΔE). METH has the highest inhibition efficiency because it had the highest HOMO energy and low (ΔE) values, and it was most capable of offering electrons. CYS has the lowest $E_{HOMO}$ value, also the lowest inhibition efficiency. Thus, the order of inhibition efficiency is METH > CYSH > CYS.

Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

**Supplementary Information**

Supplementary information (output results of quantum chemical calculations) is available free of charge, on correspondence to the author on request.
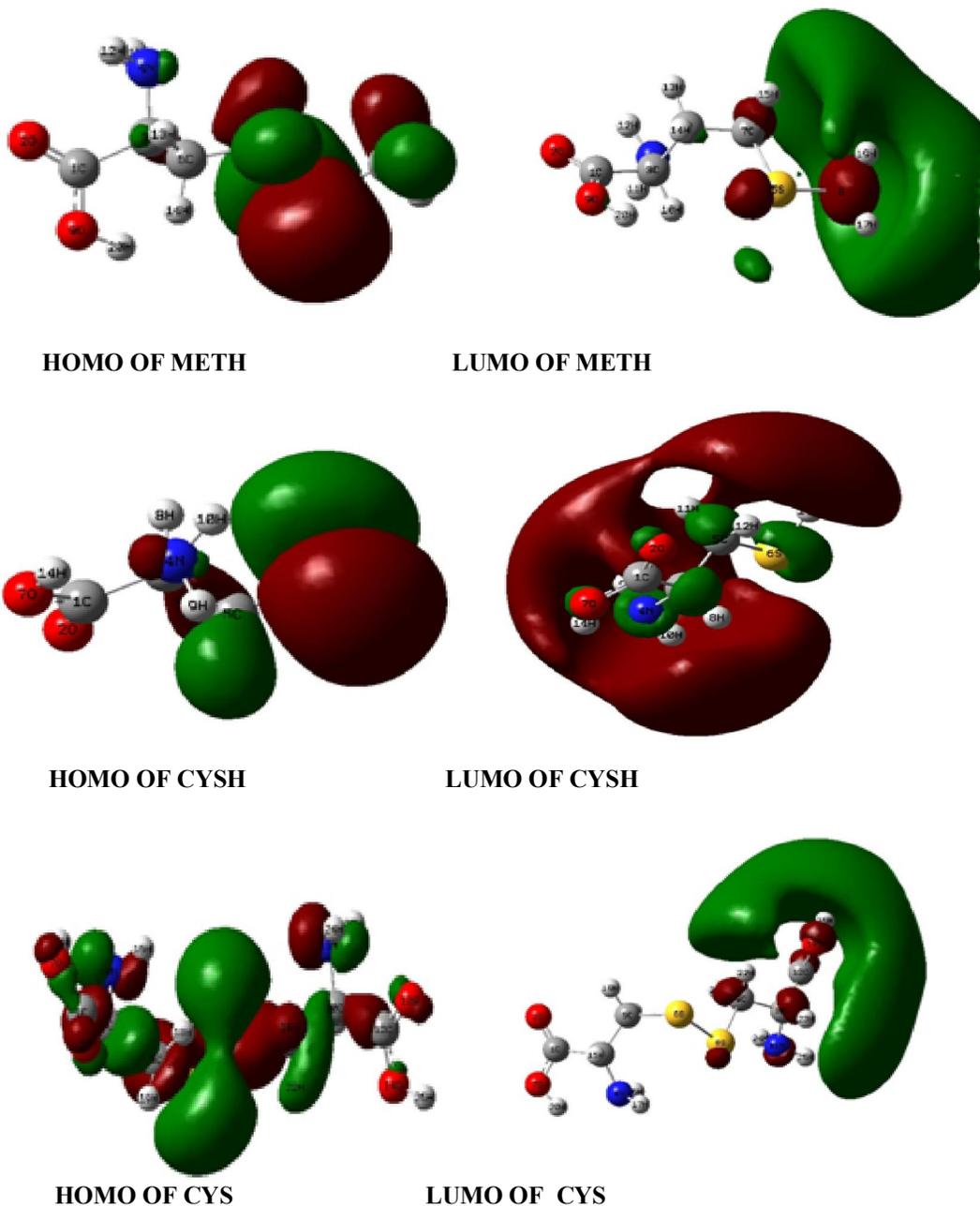
HOMO OF METH                    LUMO OF METH

HOMO OF CYSH                    LUMO OF CYSH

HOMO OF CYS                     LUMO OF  CYS

**Figure 3. Frontier molecular orbital diagrams of METH, CYSH and CYS by the RHF/6-31+g(d) model chemistry**

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