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Determination of corrosion inhibition effects of amino acids: Quantum chemical and molecular dynamic simulation study

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ABSTRACT

Amino acids are biologically important organic compounds in the human body which contain two important functional groups namely: $-NH_2$ (amine) and –COOH (carboxylic acid) in their structures. In the present work, corrosion inhibitive performance amino acids such alanine (Ala), methionine (Met), aspartate (Asp), asparagine (Asn), lysine (Lys), arginine (Arg) and histidine (His) were investigated. All quantum chemical calculations related to these amino acids at the B3LYP/6-31G++(d, p) HF/6-31G++(d,p) methods were performed. Corrosion inhibition effects of the subject amino acids were discussed not only in the gas phase but also in the water phase, acetic acid and formic acid. Furthermore, molecular dynamic simulations employing Monte Carlo sampling approach were applied to search for the most stable configuration and adsorption energies for the interaction of the amino acid corrosion inhibitors on Cu (111)/50 H_2O interface. A good correlation between theoretical data and experimental data has been obtained. Moreover, arginine that is a basic amino acid the best corrosion inhibitor among amino acids, considered in this study.

1. Introduction

Amino acids [1] are biomolecules that have vital significance to all organism and they are the building blocks of proteins and many essential substances like neurotransmitters, hormones and nucleic acids. These molecules are considered in many scientific researches related to nutrition, medicine and plant protection. The term amino acid are used for molecules that contain both amino ($-NH_2$) and carboxyl (–COOH) groups. Amino acids can be schematically represented as follows (Fig. 1):

Except for glycine, α-amino acids have side chains (symbolized by R). The inductive effect of side chain in the amino acids has a decisive influence on reactivity of amino acids. As a matter of fact, amino acids that have both amino group and acidic carboxyl group combine many properties and reactions of both amines and carboxylic acids. Additional groups in side chains of some amino acids may add more different properties to the amino acid in terms of reactivity. In the recent times, amino acids were investigated even as corrosion inhibitors because of their superior reactivities.

Corrosion studies have attracted considerable interest in the areas of material chemistry and industrial chemistry [2–5]. The corrosion that is undesirable process is the progressively destruction of especially metals by chemical reaction with various molecules in their environment. With another statement, this chemical process can be expressed as electrochemical oxidation of metals in reaction with an oxidant such as oxygen. One of the most extensive methods is use of organic corrosion inhibitors. Corrosion inhibitors are substances that preserve metals by preventing or reducing the corrosion process. The most effective inhibitors are π-systems and heterocyclic organic compounds that contain atoms such as O, N, P or S [6,7].

In several experimental studies, the inhibition effectiveness of some amino acids was investigated against some metals [8–10]. A good corrosion inhibitor should be easy electron donor, high purity at low cost and non-toxic. Amino acids have these features that were stated. In this context, the molecular structure of inhibitors plays an important role. For instance, methionine derivatives contain sulphur atom in their structure and sulphur-containing structures are located in the class of soft bases as a result of Hard and Soft Acid–Base (*HSAB*) principle. Soft chemical species do not show the resistance against electron cloud polarization or deformation. So they give easy electron to metals and are good corrosion inhibitors. The corrosion study of Ashassi-Sorkabi [11] can be given as an example on this topic. In their study, it is reported that methionine which contains S atom is successful corrosion inhibitor for aluminium. Corrosion inhibition effectiveness of molecules can be compared with the help of various electronic structure parameters. The most popular parameters among these are the eigenvalues of highest-occupied (*HOMO*) and

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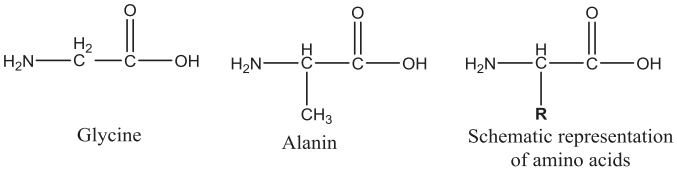

Fig. 1. The structure of some amino acids and schematic representation of amino acids.

lowest-unoccupied (*LUMO*) molecular orbitals, *HOMO–LUMO* gap electronegativity and chemical hardness.

In the recent times, the use of quantum chemical methods in the estimation of potential corrosion inhibitors has been extremely useful. Quantum chemical parameters which are based on the Density Functional Theory such as chemical hardness, electronegativity, chemical potential, nucleophilicity, electrophilicity have been the guide for investigating the agreement with experimental data of the results of computational chemistry works. Of course, it should be expressed that one of the biggest contributions to computational chemistry studies is that contribution which Koopmans theorem [12] provides. In addition to this information, to talk in detail Hard and Soft Acid–Base (HSAB) Theory [13–15] is required. HSAB theory was introduced in 1960s by Pearson as a result of a study related to Lewis acid–bases. According to this theory, Lewis acid and bases were classified as hard and soft and it should be stated that hard acids prefer to coordinate hard bases and soft acids prefer to coordinate soft bases. The reason for these preferences is that hard–hard interaction is mainly electrostatic and soft–soft interaction is mainly covalent interaction. HSAB theory should be considered in the corrosion studies because corrosion inhibitors are Lewis bases. Nowadays, HSAB theory that is an important development in the quantum chemistry provides utilities in the many theoretical and experimental studies related to corrosion inhibitors, complex stability, chemical equilibrium, gravimetry as well as precipitation titrations.

In the conceptual Density Functional Theory (*DFT*) [16,17], the reactivity indexes such as electronegativity (χ) [18,19], chemical hardness (η) [20] and chemical potential (μ) are defined as derivatives with respect to number of electron (N) of the electronic energy (E) at external potential (υ). The mathematical operations related to these concepts are given as follows [21].

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{\upsilon(r)} \tag{1}$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{\upsilon(r)} \tag{2}$$

Pearson and Parr were presented operational and approximate definitions using the finite differences method depending on electron affinity (A) and ionization energy (I) of any chemical species (atom, ion or molecule) for chemical hardness, softness (σ) electronegativity and chemical potential [22–24].

$$\chi = -\mu = \left(\frac{I+A}{2}\right) \tag{3}$$

$$\eta = \frac{I-A}{2} \tag{4}$$

$$\sigma = \frac{1}{\eta} \tag{5}$$

Electrophilicity may be stated as the measure of reactivity towards attracting electrons from a nucleophile of a chemical species [25]. Parr and co-workers proposed an electrophilicity index [26] considering electron transfer process between an electrophile that is immersed into sea of electron and a sea of free electron at zero temperature and zero chemical potential. According to Parr's study, electrophilicity index (ω) is given by the following equation in accordance with suggestion of Maynard and co-workers [27]. Nucleophilicity (ε) is physically inverse of electrophilicity ($1/\omega$).

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{6}$$

$$\varepsilon = \frac{1}{\omega} \tag{7}$$

The parameters which were defined above are the most important parameters considered in scientific researches about corrosion inhibition. It should be clearly that these parameters provides information about electron donating ability of chemical species and the most notable feature of a corrosion inhibitor is its electron donating ability to metals because electron donor chemical species prevent the oxidation of metals.

As a result of Koopman's theorem, the electronic structure parameters like chemical hardness, chemical potential and electronegativity have been associated with Molecular Orbital Theory (MOT). This theorem specifies that the energy of the highest occupied molecular orbital (E_{HOMO}) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}) correspond to ionization energy and electron affinity, respectively.

$$\chi = -\mu = \left(\frac{I+A}{2}\right) = \frac{E_{HOMO} + E_{LUMO}}{2} \tag{8}$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{9}$$

We have realized from experience that the use of standalone electronic properties is not sufficient to predict the trend of the inhibition performance of the investigated inhibitors in spite of its success in exploring the mechanism of inhibitor reactivity. In fact, in many cases direct correlation between the computed electronic parameters and experimental inhibition efficiencies cannot be established for some set of inhibitors. Therefore, it is imperative to carry out rigorous modelling of the direct interaction of the inhibitors with copper in the presence of water to mimic the real experimental condition using molecular dynamics simulations.

The goal of the present work is therefore to investigate the effectiveness of some amino acids such as alanine, methionine, asparagine, aspartate, lysine, arginine and histidine using quantum chemical calculation and molecular dynamics simulations approach. This theoretical tool is further used to determine the best corrosion inhibitor among them.

2. Quantum chemical calculation method

It should be stated that DFT methods are widely used in computational chemistry studies because these methods have become very popular in recent times. The input files of amino acids were prepared with Gauss View 5.0.8 [28]. The calculation in the gas phase were made using HF and DFT/B3LYP methods with LANL2DZ, 6-31++G (d, p), CEP-316 basis sets. Taking advantage from results obtained in the gas phase, the most appropriate basis sets among them for alanine (Ala), methionine (Met), aspartate (Asp), asparagine (Asn), lysine (Lys), arginine (Arg) and histidine (His) are selected. Later on, the selected methods and basis sets (B3LYP/LANL2DZ, B3LYP/6-31++G (d, p), B3LYP/CEP-31 G) [29] are applied to these amino acids not only in the gas phase but also in the water, acetic acid and formic acid. The results obtained in all phases are compared with experimental data that is given for some of these amino acids and it was suggested that arginine is the best corrosion inhibitor among these seven amino acids.

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