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# Corrosion control of copper in nitric acid solutions using some amino acids – A combined experimental and theoretical study

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ABSTRACT

Inhibition performance of three amino acids, namely L-methionine (MIT), L-methionine sulfoxide (MITO) and L-methionine sulfone (MITO2), as corrosion-safe inhibitors for copper surface in 1.0 M nitric acid was investigated by weight loss, dc polarization and ac impedance techniques. A significant decrease in the corrosion rate of copper was observed in the presence of the investigated compounds. The reactivates of the compounds under investigation were analyzed through Fukui functions, to explain their inhibition performance. Simulation techniques incorporating molecular mechanics and molecular dynamics were used to simulate the adsorption of L-methionine derivatives, on copper (1 1 1) surface in nitric acid.

## 1. 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. Nitrogen and sulphur-containing organic heterocyclic compounds may act as inhibitors for copper dissolution due to the chelating action of heterocyclic molecules and the formation of a physical blocking barrier on the copper surface [2]. Among organic heterocyclic compounds, benzotriazole (BTA) is well known as an effective inhibitor of copper corrosion in neutral/alkaline solutions [3,4]. It is generally accepted that its inhibition mechanism in neutral and alkaline solution is the adsorption of a single BTA molecules on the copper surface and the formation of a polymeric film of a ($Cu^+$BTA) complex [5]. However, in an acidic solution, BTA exists predominantly as a protonated species, $BTAH^+$. This protonated species is less strongly chemisorbed on the copper surface, as the metal is thought to be positively charged in acidic solution [6]. This is in turn leads to a decrease in the inhibition efficiency of BTA in acidic solution. Some other heterocyclic compounds have also been shown to be effective inhibitors for the corrosion of copper and its alloys. However, a very important disadvantage of these heterocyclic compounds is their toxicity and most of them cannot be biodegraded [7]. This lack of biodegradability leads to the emission of industrial waste water carrying a large amount of toxic material to public water ways.

There is a need for new inhibitors for copper corrosion in acidic media. A possible solution to this problem is to find new ecologically, friendly green corrosion inhibitors. Natural products extracted from plant sources [8–12], as well as some non toxic organic compounds, which contain polar functions with nitrogen, oxygen and/or sulphur in conjugated systems in their molecules [8–20], have been effectively used as inhibitors in many corrosion systems. Amino acids are attractive as corrosion inhibitors because they are relatively easy to produce with high purity at low cost and are soluble in aqueous media. Methionine derivatives are sulphur-containing amino acids. Methionine itself is investigated as possible corrosion inhibitor for mild steel [21–25] and for low carbon steel [26]. Ashassi-Sorkhabi et al. [27] 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.

On continuation of our work on using L-methionine derivatives as possible green corrosion inhibitors for various metals in acid media [28], the aim of the present work is to study the influence of some selected sulphur-containing amino acids, namely L-methionine (MIT),

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L-methionine sulphoxide (MITO) and L-methionine sulfone (MITO2), on the inhibition of copper corrosion in 1.0 M $HNO_3$ solutions using chemical (weight loss), electrochemical techniques (potentiodynamic polarization and electrochemical impedance spectroscopy) as well as explicit solvent simulations using molecular dynamics and quantum chemical calculation to explore the adsorption mechanism of these amino acids on copper surface (1 1 1). In addition, as the electronic structure of these amino acids and their correlation with inhibitor efficiencies will be sought.

## 2. Experimental

The weight loss measurements were carried out in a 250 ml capacity glass beaker placed in a thermostat water bath. The solution volume was 100 ml. The used copper coupons (Puratronic, 99.999%, Johnson Matthey Chemicals) had a rectangular form (length = 2.5 cm, width = 2 cm, thickness = 0.05 cm). The coupons were weighed and suspended in 100 ml of an aerated 1.0 M $HNO_3$ solution containing L-methionine derivatives at the desired concentrations for 36 h exposure period of time at 25 ± 1 °C.

At the end of the tests, the coupons were taken out, washed with bi-distilled water, degreased with acetone, washed again with bi-distilled water, dried, and then weighed using an analytical balance (precision: ±0.1 mg). Three measurements were performed in each case and the mean value of the weight loss has been reported. The standard deviation of the observed weight loss was ±1%. The corrosion rate, $w$ (expressed in mg $cm^{-2}$ $h^{-1}$) as well as the inhibition efficiency ($\upsilon_w$%) over the exposure time period were calculated according to the following equation:

$$\upsilon_w\% = \left(1 - \frac{w}{w_o}\right) \times 100 \quad (1)$$

where $w_o$ and $w$ are the weight loss without and with L-methionine derivatives, respectively.

A cylindrical copper rod was welded with iron-wire for electrical connection and mounted in Teflon with an active flat disc shaped surface of (0.28 $cm^2$) geometric area, to contact the test solution. Prior to each experiment, the copper electrode was abraded using different grit sizes emery papers up to 4/0 grit size to remove the corrosion products if any, formed on the surface. The copper electrode was etched in 7 M $HNO_3$ solution for 15 s, cleaned in 18 MΩ water in an ultrasonic bath for 5 min., and subsequently rinsed in acetone and bi-distilled water, and immediately immersed in the test solution.

The L-methionine derivatives are presented in Fig. 1. All of these compounds were obtained from Aldrich chemical co. They were put in the 1.0 M $HNO_3$ (Fisher Scientific) without pre-treatment at concentrations of 0.1, 0.5, 1.0 and 5.0 mM. The electrode was immersed in these solutions for 1 h before starting measurements, the time necessary to reach a quasi-stationary value for the open circuit potential.

A conventional electrochemical cell of capacity 250 ml was used containing three compartments for working, platinum mesh counter and reference electrodes. A Luggin-capillary was also included in the design, the tip of which was made very close to the surface of the copper electrode to minimize IR drop. The reference electrode was a saturated calomel (SCE) used directly in contact with the test solution. The measurements were carried out in aerated stagnant 1.0 M $HNO_3$ solutions at 25 °C (using water thermostat ±1 °C) without and with various concentrations (0.1–5 mM) of L-methionine derivatives, as possible corrosion inhibitors. All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification. For each run, freshly prepared solutions as well as a cleaned set of electrodes were used.

Tafel polarization curves were obtained by changing the electrode potential automatically from −280 to +200 m $V_{SCE}$ with a scan rate of 1 mV $s^{-1}$. Impedance measurements were carried out in a frequency range of 10 kHz to 20 mHz and with amplitude of 5 mV peak-to-peak using ac signals at open circuit potential. Measurements were performed with a Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry framework system based on the ESA400, Gamry applications that include DC105 for dc corrosion measurements, EIS300 for impedance measurements to calculate the corrosion current and the Tafel constants along with a computer for collecting the data. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.

## 3. Theory and computational details

In order to support experimental data, theoretical calculations were conducted in order to provide molecular-level understanding of the observed experimental behavior. The major driving force of quantum chemical research is to understand and explain the functions of these L-methionine derivatives in molecular terms. Among quantum chemical methods for evaluation of corrosion inhibitors, density function theory, DFT has shown significant promise [29] and appears to be adequate for pointing out the changes in electronic structure responsible for inhibitory action. It is expected that the L-methionine derivatives molecules in solution behave differently from that in vacuum. The solvent effect on molecular structure of solute can be studied by a model which is known as polarized continuum model (PCM) [30]. In this model, solvent is treated as an expanse of dielectric media and the solute as a trapped molecule in a cavity surrounded by solvent. All calculations related to the inhibitor/Cu surface obtained by DFT study are done in water solvent molecules.

There is no doubt that the recent progress in DFT has provided a very useful tool for understanding molecular properties and for describing the behavior of atoms in molecules. DFT methods have become very popular in the last decade due to their accuracy that similar to other methods in less time and with a smaller investment from the computational point of view. In agreement with the DFT, the energy of the fundamental state of polyelectronic systems can be expressed through the total electronic density, and in fact the use of the electronic density instead of the wave function

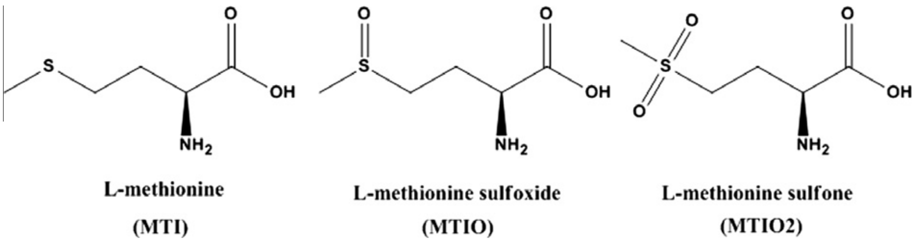

**Fig. 1.** Molecular structures of the L-methionine derivatives.