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Computational study of some triazole derivatives (un- and protonated forms) and their copper complexes in corrosion inhibition process

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ABSTRACT

Three triazoles compounds used as corrosion inhibitors for copper in acidic medium, namely: 1,2,4 triazole (TR), 3-amino 1,2,4 triazole (3 ATR) and 3,5-diamino 1,2,4 triazole (3,5 DATR) have been studied theoretically in aim to investigate the correlation between its molecular reactivity indicators and the corresponding inhibition efficiency. All quantum chemical calculations at the B3LYP/6-31+G(d,p) method were performed with and without solvent effect. In the present paper, not only the neutral inhibitors has been studied, but also the first and the second protonation forms. A good correlation between theoretical and experimental data has been obtained both in gas and aqueous phases, notably for unprotonated inhibitors. Also, the interaction energy between inhibitors and copper has been calculated.

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1. Introduction

Corrosion inhibitors are substances that preserve metals by preventing or reducing the corrosion rate process [1]. The most effective organic inhibitors are π-system and heterocyclic organic compounds that contain atoms such as O, N, P or S which facilitated its adsorption on the metal surface [1,2]. Among several categories of azole compounds, there are the triazole class [3]. The structure of these molecules contains three nitrogen atoms in its penta ring, and are well known as the non-toxic chemicals compounds [2]. For these reasons, they have been the subject of many studies on their ability to act as corrosion inhibitors for various metals and alloys [2,4–6]. The effect of 1,2,4-triazoles compounds with and without introduction of amino group ($-NH_2$) against the corrosion behavior of copper in molar sulfuric acid solution has been reported earlier [4]. It was shown that these compounds act as corrosion inhibitors with an inhibition efficiency upper to 65%.

In the last decade, the theoretical chemistry was widely used on the corrosion inhibition research, that is attributed to the improvement of hardware and software capabilities [7,8]. Several quantum methods and molecular modeling techniques have been performed, in one hand to associate the inhibition efficiency of the inhibitors with their molecular properties, such as, HOMO energy, LUMO energy, energy of gap (ΔE), chemical hardness (η), total negative charge (TNC) … etc. In other hand, they are used to guess a possible mechanism of their interactions with the metal surface [9–12].

In acidic environment, the triazoles also interact with the acidic solution leading to the possibility of co-existence of both protonated and non-protonated species of the triazole [13–15]. For this propose, it's important to considerate, also, the protonated form to understand the obtained inhibition efficiency (IE(%)). In this context, in addition to the first protonation state, we will extend our computational study to the second protonation state of these species in order to complete the vision on their activities as corrosion inhibitors.

The object of this work is to investigate theoretically how the introduction of amino groups into Triazole molecular structure affects its corrosion inhibition ability for copper. In addition, we are interested by fitting a possible correlation between this inhibition ability and calculated molecular reactivity indicators, both for neutral and protonated inhibitors. Fig. 1 represents the investigated inhibitors: 1,2,4 triazole (TR), 3-amino 1,2,4 triazole (3 ATR) and 3,5-diamino 1,2,4 triazole (3,5 DATR). Furthermore, the calculations were conducted on copper interactions with various molecular sites of the triazoles, namely nitrogen atoms.

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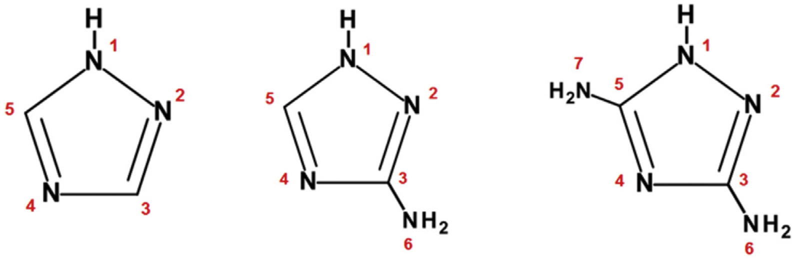

(TR) (3 ATR) (3,5 DATR)

Fig. 1. Chemical structure and atomic numeration of studied Triazolic compounds, with their abbreviations which will use subsequent.

2. Quantum chemical calculations

To investigate the relationship between molecular structures of the inhibitor and their inhibition effect, quantum chemical molecular calculations have proved to be a powerful tool for studying corrosion inhibition mechanism. Some quantum chemical parameters can be related to the interactions of metal-inhibitor [8,16]. For this propose, the Density Functional Theory (DFT) is used with the Beck's three parameter exchange functional along with the Lee-Yang-Parr non local correlation functional (B3LYP), employing 6-31+G(d,p) as basis sit which was comfortable to get a good geometry optimization [9,17,18]. The full optimized geometry structure was checked by non-presence of imaginary vibration frequencies. Afterwards, several quantum chemical parameters of isolated molecules both in gas and aqueous phase for neutral and protonated forms were calculated, namely: the energy of highest occupied molecular orbital (E_{HOMO}), the lowed unoccupied molecular orbital energy (E_{LUMO}), gap energy between E_{LUMO} and E_{HOMO} (ΔE) and dipole moment (μ). Further, Mulliken charges distribution, total negative charge (TNC), electrostatic potential maps and the molecular orbitals were worked out.

To complete the vision on the inhibition property of these molecules, other molecular reactivity indicators were calculated. Electronegativity (χ) and chemical hardness (η) of the inhibitor molecule are given by the relations (**1**) and (**2**). These parameters are based on the first and second partial derivation of the total energy of system with respect to electron number (N) at constant external potential (ν) [19].

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{\nu} \quad (1)$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu} \quad (2)$$

Pearson and Parr were presented operational and approximate definition using the finite difference method for the first and second derivatives and negative of the HOMO and LUMO molecular orbitals, which in turn are used as left and right derivatives of $\frac{\partial E}{\partial N}$, respectively. The absolute chemical hardness is given by Refs. [20,21]:

$$\eta \approx 0.5\ (E_{LUMO} - E_{HOMO}) \quad (3)$$

While absolute electronegativity is approximated by Ref. [20]:

$$\chi \approx -0.5\ (E_{HOMO} + E_{LUMO}) \quad (4)$$

In agreement with Pearson [22], the fraction of electrons transferred (also known as the “electron-donating ability” [23,24]) between the inhibitor molecule and the metallic surface is given by:

$$\Delta N = \frac{\chi_{metal} - \chi_{molecule}}{2\ (\eta_{metal} + \eta_{molecule})} \quad (5)$$

where, χ_{metal} and $\chi_{molecule}$ denote the absolute electronegativity of metal and the inhibitor molecule, respectively, while η_{metal} and $\eta_{molecule}$ denote the absolute hardness of metal and the inhibitor molecule. In our study, theoretical values of χ_{metal} and η_{metal} for copper were 4.48 eV mol^{-1} and 0 eV mol^{-1}, respectively [17]. So, the defined ΔN measures the transfer of electrons from molecule to metal surface if $\Delta N > 0$ and vice versa if $\Delta N < 0$ [25].

In order to investigate the preferred adsorption site for the interaction between the triazole compounds and the copper atom, the interaction energies (noted E_{int}) were calculated by the Eq. (6), where E_{Cu} is the total energy of the copper atom and $E_{Inhibitor}$ is the total energy of the inhibitor compound. When $E_{(Cu-Inhibitor)}$ represents the total energy of new formed system between the compound and the copper [26,27].

$$E_{int} = E_{(Cu-Inhibitor)} - (E_{Inhibitor} + E_{Cu}) \quad (6)$$

All quantum calculations were conducted by using the Gaussian 09 software package for Windows [28] via dual core 2.40 GHz processor (Intel CORE i5). For the aqueous phase, the solvent effect was treated by Polarized Continuum Model (PCM) within the Self-Consistent Reaction Field method (SCRF) [29] using water as solvent.

3. Results and discussions

3.1. *Neutral inhibitors forms*

In this study, quantum chemical calculations were conducted by DFT method (B3LYP/6-31+G(d,p)) either in gas or aqueous phase. In aim to found a correlation between the electronic structure of studied compounds and their inhibition effectiveness, several electronic parameters were calculated on the founded optimize geometries. The energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE), hardness (η), electronegativity (χ), electron-donating ability (ΔN), dipole moment (μ) and total negative charge (TNC) parameters with the experimentally inhibition efficiencies (acquired from EIS technique, at 10^{-3} M [4]), are given in Table 1. Firstly, as shown, the presence of water as solvent does not change much the HOMO and LUMO energy values, except the LUMO energy of 3,5 DATR. However, the dipole moment increased going from gas to aqueous phase, due to molecular polarization generated by the effect of solvents molecules interaction [9].

For the association of these parameters with inhibitor effectiveness, the E_{HOMO} is often associated with the electron donating

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