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The investigation of corrosion inhibition efficiency on some benzaldehyde thiosemicarbazones and their thiole tautomers: Computational study

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ABSTRACT

Quantum chemical calculations using three methods, Hartree–Fock (HF), Møller–Plesset (MP) and density functional theory (DFT/B3LYP) method with SDD, 6−31G(d,p) and 6−31++G(d,p) basis sets are performed some benzaldehyde thiosemicarbazones and their thiole tautomers. The results of the quantum chemical calculations and experimental IE% which are belong to thione tautomers are subjected to correlation analysis and indicate that their inhibition effect are closely related to some quantum chemical parameters. The active sites are determined by using MEP diagrams, proton affinities and Fukui functions. The theoretically obtained results are found to be consistent with the experimental data which are reported for thione tautomers.

1. Introduction

Corrosion is an electrochemical process and plays an important role in economics, industry, human life and safety for metals. Therefore, the protection of metal against corrosion is an important industrial and scientific topic. Some organic compounds have been widely used as corrosion inhibitors for metal or alloys in acid medium. The most effective corrosion inhibitors are those compounds containing heteroatoms as nitrogen, oxygen and sulphur atoms as well as aromatic rings [1–9]. Thiosemicarbazones which are important compounds in many fields have been reported earlier as corrosion inhibitors for steel. Recently, Yang and co-workers experimentally found and the thiocarbazone derivatives show inhibitive properties for mild steel in HCl solution [10–14].

Benzaldehyde thiosemicarbazone and its derivatives which are important compounds in many fields have been reported earlier as corrosion inhibitors for mild steel. Recently, Abd-El-Rhman and co-workers [15] have investigated experimentally the inhibition efficiencies of three benzaldehyde thiosemicarbazone derivatives as shown in Fig. 1, namely, benzaldehyde thiosemicarbazone (BTSC), para-chlorobenzaldehyde thiosemicarbazone (PCIBTSC), and 4-(dimethylamino)benzaldehyde thiosemicarbazone (4DMBTSC) for the corrosion of mild steel in 3 M phosphoric acid. The inhibition efficiency of an inhibitor is mainly conducted by experimental methods, such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) [15]. But these experimental methods are high-cost, time-consuming, and deficient in elucidating inhibition mechanism. The relationships between the quantum chemical parameters and corrosion inhibition of those compounds have not been studied yet.

Experimental studies are useful in explaining the inhibition efficiency of corrosion inhibitors but these studies are mainly expensive and time consuming. Additionally to experimental studies, properties of inhibitors can be provided by computational chemistry methods without consuming energy, chemical and time. Computational chemistry methods are reliable in explaining the inhibition efficiency of corrosion inhibitors [16–23] and there are many published papers about density functional theory (DFT) studies of organic corrosion inhibitors [24–28,14]. As theoretically, quantum chemical parameters (provide by using computational chemistry methods) such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap (ΔE_{GAP}), sum of total negative charges (TNC), hardness (η), softness (σ), proton affinities (PA) and molecular volume (MV) can be used to provide the inhibition efficiency ranking of corrosion inhibitors. The aim of the present work is to investigate the effects of different structures (thione and thiole tautomers) of BTSC, PCIBTSC and 4DMBTSC by using

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1876-1070/

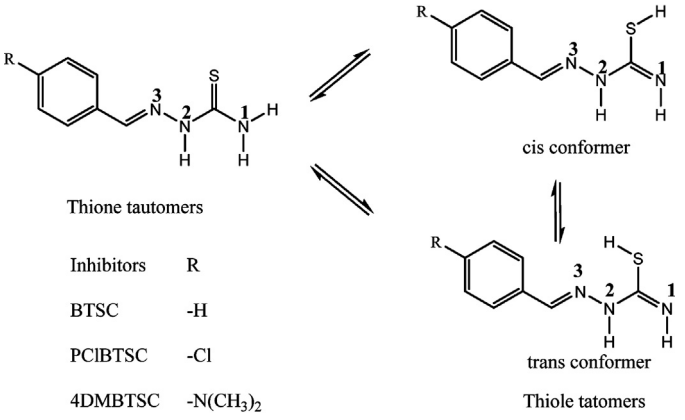

Fig. 1. Molecular structure of investigated benzaldehyde thiosemicarbazones and two conformers (cis and trans) of thiole tautomers.

computational chemistry methods. We also considered the effect of water as solvent on the calculated parameters, since corrosion commonly occurs in the liquid phase. Quantum chemical parameters and experimental inhibition efficiencies are subjected to the correlation analysis. The new formula is derived to investigate the inhibition efficiency of benzaldehyde thiosemicarbazone compounds.

2. Computational method

All calculations were performed using Gaussian 09 package programme [29]. The visualization of results was done using GaussView 5.0.8 [30]. The molecular structures of the investigated compounds, which are represented in Fig. 1, were fully optimized by using Hartree–Fock (HF), density functional theory method (DFT-B3LYP), Møller–Plesset (MP2) methods with SDD, 6−31G(d,p) and 6−31++G(d,p) basis set in gas phase and water. The HF approximation for the total interacting system was taken as the zero-order approximation. The second-order MP (MP2) theory could be a straightforward option by the perturbational inclusion of electron pair–pair interactions. The B3LYP is hybrid DFT functions and combination of exchange and correlation functional [31,32]. The geometry optimizations were considered to be complete when the stationary point was located. The optimized structures were confirmed to be true minima by frequency analysis (no imaginary frequencies). The investigated thione and thiole tautomers are easily protonated in acidic medium. Therefore the calculations were extended to the protonated forms of the each tautomer under study. The solvent effect on the molecular structures of the investigated compounds was studied by a model known as polarized continuum model (PCM) [33]. Some quantum chemical parameters (ΔE_{GAP}, TNC, η, σ, ω, N, and ΔN) were calculated with Eqs. (1)–(7), respectively [34–40]:

$$E_{GAP} = E_{LUMO} - E_{HOMO} \tag{1}$$

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

$$\sigma = \frac{1}{\eta} \tag{3}$$

$$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2} \tag{4}$$

$$\omega = \frac{\chi^2}{2\eta} \tag{5}$$

$$N = \frac{1}{\omega} \tag{6}$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh.}}{[2(\eta_{Fe} + \eta_{inh.})]} \tag{7}$$

Using a theoretical value, χ_{Fe} = 7.0 eV/mol and value of η_{Fe} = 0 eV/mol for iron according to Pearson's electronegativity scale assuming that for a metallic bulk ($-E_{HOMO} = -E_{LUMO}$), because they are softer than neutral metallic atoms.

3. Results and discussion

3.1. Non-protonated inhibitors

The study of Schiff's base inhibitors is an attractive topic. Because the planarity structure and lone pair of electrons present on the N atoms in the presence of >C=N– groups, the Schiff base inhibitors show good corrosion inhibition efficiencies. Considering that BTSC, PClBTSC, 4DMBTSC molecules can coexist in two tautomeric forms in solutions: thione forms and thiole forms (cis-thiole and trans-thiole). Investigated inhibitors thione tautomers have one conformation while their thiole tautomers could be cis (S–H moiety eclipsing C=N bond), trans (S–H moiety eclipsing C–N bond). Quantum chemical calculations are performed on the mentioned inhibitors. The optimized structures of non-protonated inhibitors are presented in Fig. 2. Mentioned quantum chemical parameters are calculated in each level and compared with inhibition efficiencies of inhibitors. According to this comparing analyses, the experimental inhibition efficiencies are more appropriate with MP2 results than other methods. Therefore quantum chemical parameters are given in Table 1, supp. Tables S1 and S2 for MP2, HF and B3LYP methods, respectively.

Experimental inhibition efficiencies have been obtained by Rhman and co-workers in 2012 [15]. According to their report, the inhibition efficiency ranking has been given as follows:

4DMBTSC(93%) > BTSC(86%) > PClBTSC(43%)

Experimental inhibition efficiencies have been obtained with electrochemical impedance parameters at 1.5×10^{-4} M inhibitors. The agreements are investigated between quantum chemical parameters and the above ranking. The most appropriate results are obtained at MP2/6−31++G(d,p) level in gas phase. Therefore, this level is taken into account for the ranking of quantum chemical parameters and other calculations.

E_{HOMO} is a quantum chemical parameter and high value of E_{HOMO} indicates the tendency of electron transfer to appropriate acceptor molecule. If E_{HOMO} is decisive for the inhibitor properties, the inhibition efficiency ranking of investigated inhibitors should be:

4DMBTSC > cis-4DMBTSC > trans-4DMBTSC > BTSC > *cis-BTSC* > *PClBTSC* > *cis-PClBTSC* > *trans-BTSC* > *trans-PClBTSC*

There is an agreement between ranking of E_{HOMO} at MP2/6−31++G(d,p) level in gas phase and experimental result. The energy of LUMO indicates the ability of the molecule to accept electrons. So, the lower the value of E_{LUMO}, the more probable that the molecule accepts electrons. According to the E_{LUMO} values, the inhibition efficiency ranking should be:

PClBTSC > trans-PClBTSC > cis-PClBTSC > BTSC > trans-BTSC > *4DMBTSC* ≈ *trans-4DMBTSC* > *cis-BTSC* > *cis-4DMBTSC*

The E_{LUMO} ranking shows that the LUMO energy of PClBTSC is the lowest energy. Because this inhibitor contains electron withdrawing group (–Cl), this result enhances the accepting