

Quantum chemical study on the inhibition efficiencies of some sym-triazines as inhibitors for mild steel in acidic medium



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ABSTRACT

Quantum chemical calculations using density functional theory (DFT) at the B3LYP/6-31++G(d,p) basis set level were performed on five sym-triazines used as corrosion inhibitors for mild steel in acidic medium to determine the relationship between molecular structure and their percentage inhibition efficiencies. The results of the calculations and experimental IE% were subjected to correlation analysis and indicate that their inhibition effect are closely related to E_{HOMO} , E_{LUMO} , energy gap, hardness, softness, electronegativity and the fraction of electrons transferred were calculated. The theoretically obtained results were found to be consistent with the experimental data reported.

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1. Introduction

Corrosion plays a very important role in diverse fields of industry and, consequently, in the economy [1–5]. One of the most economical and effective ways to protect from corrosion is to use the corrosion inhibitors. A corrosion inhibitor is a substance used in a very small amount that effectively reduces the corrosion rate. Several classes of organic compounds are widely used as corrosion inhibitors for metals in acid environments. Many efficient inhibitors are heterocyclic organic compounds consisting of a π -system and/or containing O, N, or S heteroatoms [6–10]. Generally, N-heterocyclic compounds are considered to be the most effective corrosion inhibitors. It has been reported that N-containing inhibitors exert their best efficiencies in hydrochloric acid [11–13]. The property to inhibit the corrosion of these compounds exert their inhibition by adsorption on the metal surface through N heteroatom, as well as those with triple or conjugated double bonds or aromatic ring in their molecular structures. Furthermore, the inhibition efficiency of an inhibitor depends not only on the characteristic of the environment in which it acts, the nature of the metal surface but also on the structure of the inhibitor itself which includes the number of adsorption active centers in the molecule, the distribution of charge over the whole inhibitor molecule, the molecular size, the formation of metallic complexes and aggressive media. The inhibition efficiency of an inhibitor is mainly conducted by experimental methods, such as weight loss assessment, polarization curves and electrochemical impedance spec-

troscopy (EIS), scanning electronic microscope (SEM), and X-ray energy dispersive spectroscopy (EDS). But these experimental methods are high-cost, time-consuming, and deficient in elucidating inhibition mechanism [14–16].

Quantum chemical methods are usually used to explore the relationship between the inhibitor molecular properties and its corrosion inhibition efficiency [17–20]. With these methods, the capability of inhibitor molecules to donate or accept electrons can be predicted with analysis of global reactivity parameters, such as energy gap (ΔE) between HOMO and LUMO, dipole moment (μ), total energy (TE), electronegativity (χ), hardness (η), softness (σ), the fraction of electrons transferred (ΔN), etc.

Triazines which are important compounds in many fields have been reported earlier as corrosion inhibitors for steel. Recently, Shukla et al. [21] investigated experimentally the inhibition efficiencies of five sym-triazine derivatives as shown in Fig. 1, namely, (Hexahydro-1,3,5-triphenyl-s-triazine (HTT), Hexahydro-1,3,5-p-tolyl-s-triazine (HPPT), Hexahydro-1,3,5-p-methoxyphenyl-s-triazine (HPMeT), Hexahydro-1,3,5-p-aminophenyl-s-triazine (HPAT) and Hexahydro-1,3,5-p-nitrophenyl-s-triazine (HPNT)) for the corrosion of mild steel in 1N hydrochloric acid medium. The relationships between the structural parameters and corrosion inhibition of those compounds have not been studied yet. The purpose of this paper is to find a correlation between molecular and electronic structures of the investigated sym-triazine inhibitors (Fig. 1) and its inhibition efficiency. Furthermore, the interaction energies of the investigated inhibitors on the iron metal were determined to discuss the inhibition mechanism. Here, our focus will be on the evaluation of the amount of inhibition of the investigated inhibitors by comparing our theoretical results with those of experimentally measured inhibition through the

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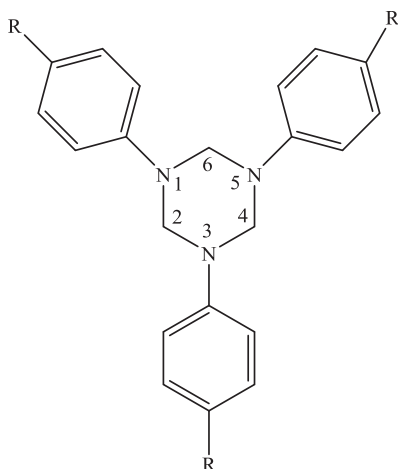


Fig. 1. The molecular structure of the investigated sym-triazines (R=H (HTT), $-\text{CH}_3$ (HPTT), $-\text{OCH}_3$ (HPMeT), $-\text{NH}_2$ (HPAT) and $-\text{NO}_2$ (HPNT)).

calculation of global reactivity parameters and interaction energies. Based on these results, a theoretical solution for inhibition efficiency evaluation of homologous inhibitor molecules may be proposed, and supportive reference for design of new inhibitors may be supplied.

2. Computational details

All calculations were performed using Gaussian 09 AML64L-Revision-C.01 [22]. The visualization of results was done using GaussView 5.0.8 [23]. The molecular structures of the investigated compounds were optimized using DFT (density functional theory) with the Lee–Yang–Parr non local correlation functional (B3LYP) using 6-31++G(d,p) basis set [24–26]. The geometry of sym-triazine-iron complexes (single iron atom) was optimized using DFT approach (B3LYP), in combination with the 6-31++G(d,p) basis set for rest atoms and effective core potential (ECP) of the LANL2DZ [27] basis set for Fe atom. 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 sym-triazines and its derivatives are easily protonated in acidic medium: Therefore the calculations were extended to the protonated forms of the sym-triazines under study.

The calculated quantum chemical parameters were generated after geometric optimization with respect to all nuclear coordinates. The ionization potential (IP) and electron affinity (EA) were calculated according to Koopman's theorem [28]. This theorem derives the relationship between the energies of the LUMO and HOMO, the ionization potential (IP), and the electron affinity (EA), respectively. EA and IP are related to E_{LUMO} and E_{HOMO} as follows:

$$\text{IP} = -E_{\text{HOMO}} \quad (1)$$

$$\text{EA} = -E_{\text{LUMO}} \quad (2)$$

Electro negativity (χ) is the measure of the power of an electron or group of atoms to attract electrons toward itself and according to Koopman's theorem; it can be estimated by using the following equation:

$$\chi = -\frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \quad (3)$$

Global hardness (η) measures the resistance of an atom to a charge transfer [29] and it is estimated using the equation:

$$\eta = -\frac{1}{2}(E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (4)$$

The inverse of the global hardness is designated as the softness, σ as follows:

$$\sigma = 1/\eta \quad (5)$$

The obtained values of χ and η were used to calculate the fraction of electrons transferred, ΔN , from the inhibitor to metallic surface [30] as follows:

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} - \chi_{\text{inh}})} \quad (6)$$

where χ_{Fe} and χ_{inh} denote the absolute electro negativity of iron and the inhibitor molecule respectively; η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. The values of χ_{Fe} and η_{Fe} are taken as 7 and 0 eVmol⁻¹ respectively [31].

The solvent effect on the molecular structures of the investigated compounds was studied by a model known as polarized continuum model (PCM) [32].

3. Results and discussion

The inhibition of steel using substituted sym-triazines (Fig. 1) as corrosion inhibitors were investigated experimentally [21]. It was found that the order of the inhibition efficiencies of these sym-triazines is HPAT > HPMeT > HPTT > HTT > HPNT.

It was observed that IE% was increased with the increasing electron-donating ability of the R groups on the phenyl ring attached nitrogen atoms in the sym-triazine ring. In sym-triazine ring, three nitrogen atoms were present as the key atoms for adsorption on the metal surface. In addition, the π -electron density of phenyl ring may also enhance the absorbability of the sym-triazine molecules.

3.1. Non-protonated inhibitors

Quantum chemical parameters obtained from the calculations which are responsible for the inhibition efficiency of inhibitors, such as the energies of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), the separation energy ($E_{\text{LUMO}} - E_{\text{HOMO}}$), ΔE , representing the function of reactivity, the net charge on the functional group, dipole moment (μ), summation of the total negative charges on atoms over the skeleton of the molecule (TNC), softness (σ), proton affinity (PA), ionization potential (IP), electron affinity (EA), electro negativity (χ) and the fraction of electrons transferred from the inhibitor to steel surface (ΔN), are collected in Tables 1 and 2 for the investigated inhibitors and their protonated species. The optimized geometries of HPAT, HPMeT, HPTT, HTT and HPNT in the non-protonated species including its HOMO and LUMO distributions are shown in Fig. 2.

According to the frontier molecular orbital theory, FMO, the chemical reactivity is a function of interaction between HOMO and LUMO levels of the reacting species [33]. The energy of HOMO is often associated with the electron donating ability of a molecule; high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. Therefore, the energy of LUMO indicates the ability of the molecule to accept electrons [34]. So, the lower the value of E_{LUMO} , the more probable that the molecule accepts electrons.

The energy gap between the LUMO and HOMO energy levels, that is, ΔE of the molecule, is another important factor to determine the inhibition efficiency. The molecules with lower ΔE values give higher inhibition efficiencies because the excitation energy gap is more polarizable and is generally associated with chemical reactivity. The E_{HOMO} values decrease in the order HPAT > HPMeT > HPTT > HTT > HPNT. That is, the highest energy E_{HOMO} is assigned for HPAT, having phenyl rings with NH_2 groups on sym-triazine ring, which is expected to have the highest corrosion inhibition among the investigated compounds. This result is caused by the fact that the electron-donating ability of $-\text{NH}_2$ group is stronger than that of further groups.

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