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Theoretical studies on the corrosion inhibition performance of three amine derivatives on carbon steel: Molecular dynamics simulation and density functional theory approaches

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ABSTRACT

Inhibition efficiencies of three amine derivatives (diethylenetriamine I, triethylenetetramine II, and pentaethylenehexamine III) on corrosion of carbon steel has been studied using the density functional theory method and molecular dynamic simulation in aqueous phase. Quantum chemical parameters such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), hardness (η), polarizability (α), dipole moment (μ), total negative charges on atoms (TNC) and molecular volume (MV) have been calculated at the B3LYP level of theory with 6-311++G** basis set. Moreover, adsorption behavior of the inhibitor molecules on Fe (110) surface has been analyzed using molecular dynamics simulation. The formation of the bonding and nonbonding interactions in systems of Fe-inhibitor molecules on Fe (110) surface followed the order III>II>I, which was in a good agreement with the experimentally determined inhibition efficiencies. The formation of bonding and nonbonding interactions in systems of Fe-inhibitor was analyzed by the radial distribution functions (RDFs). In agreement with the experimental data, theoretical results showed that the order of inhibition efficiency is III>II>I.

1. Introduction

Because of various applications of steels in industrials, for a long time protection of steels surfaces are a major concern and an important scientific topic. Some substances can be adsorbed on the metal surface and reduced the rate of corrosion [1,2]. Often, corrosion inhibition mechanism has been experimentally investigated, however, they are expensive and time-consuming [1–5]. Theoretical methods including quantum chemical calculation and molecular dynamic simulation have proved to be the most appropriate methods for elucidating the inhibition mechanism of organic inhibitors [5–7]. In the recent decades, successful researches have been carried out in the field of corrosion inhibition using different computational approaches [1,3–13]. In the quantum chemical methods, several factors and quantum chemical parameters are checked to study the corrosion inhibitive potentials of inhibitors. Also, for systems involving a relatively large number of molecules, molecular dynamics (MD) simulation as an effective tool has been often used to study the interaction of inhibitors with the metal surface [14–16]. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds [17]. Investigations of corrosion inhibiting abilities of tannins, alkaloids, organic, amino acids, and organic dyes of plant origin are of interest.

The inhibitive properties of three amine derivatives on the corrosion rate of carbon steel in cooling water systems have been experimentally investigated by Migahed et al. [18]. In the present study, inhibition effects of three amine derivatives (Fig. 1) have been investigated on corrosion of carbon steel using some quantum chemical parameters such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), hardness (η), polarizability (α), total negative charges on atoms (TNC), molecular volume (MV), dipole moment (μ). Also, the local reactivity has been studied through the Fukui indices in order to realize the possible sites of nucleophilic and electrophilic attacks. Molecular dynamics (MD) simulation, which has been proven to be very efficient in the evaluation of the interaction of organic compounds with metal surface, was used to analyze the adsorption energies of amine compounds upon the Fe (110) surface. In this study, we show that DFT along with MD can be successfully used as reliable approaches to screen organic corrosion inhibitors prior to experimental validation.

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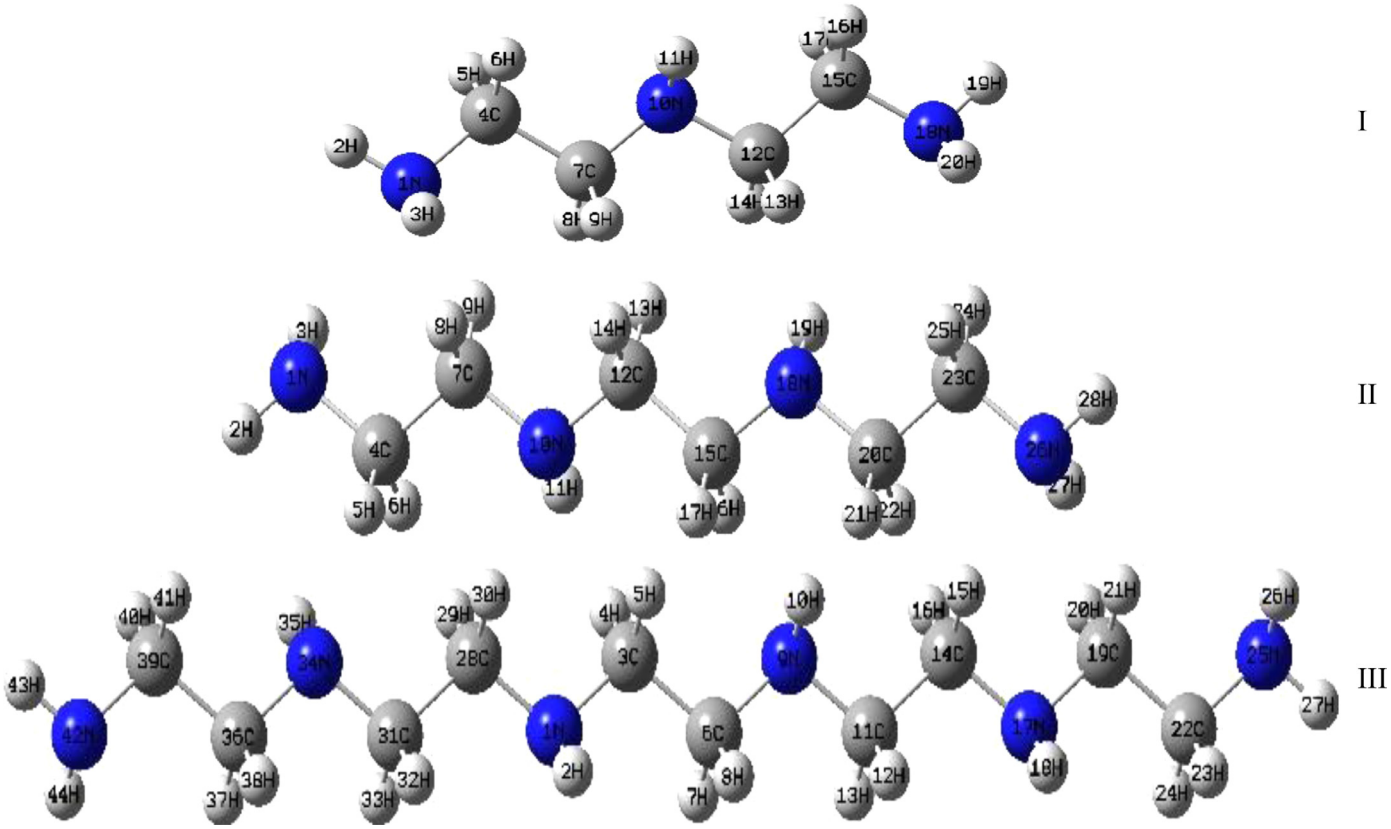

Fig. 1. The optimized structures of the studied amines.

2. Computational details

2.1. Quantum chemical calculations

Computational chemistry methods were performed using the density functional theory (DFT) method at the hybrid functional B3LYP level of theory with 6-311++G** basis set [19–21] by the Gaussian 03 series of programs [22]. The frequency analysis was performed to ensure that the researched molecules reached their respective ground state. All the frequencies are found to be positive, which reflects that the ground state optimized structures correspond to global minima. Generally, the phenomenon of electrochemical corrosion occurs in the aqueous phase, so it is necessary to consider the effect of solvent in the calculations. Hence, the polarizable continuum method (PCM) was applied in order to incorporate the effect of solvent (water) in the calculations. The self-consistent reaction field (SCRF) theory along with Tomasi's polarized continuum model (PCM) was employed for better understanding of the experimental results obtained from the aqueous solution [23].

Indexes of global electronic within the DFT of Parr, Pearson and Yang [24,25] are useful tools for understand the reactivity of molecules in their ground state. There are several parameters which can be used as global or local reactivity descriptors.

Global hardness (η) within the DFT measures the resistance of an atom to a charge transfer [24] as the second derivative of the E with respect N at $v(r)$ property (1):

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

Electronegativity χ is the measure of the power of a group of atoms to attract electrons towards itself when chemically combined with another atom [26], According to DFT it can be expressed with the Eq. (2):

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{2}$$

Where E is the electronic energy in electron volts, N is the number of electrons, and $v(r)$ is the external potential generated by the nuclei.

Using a finite difference method [24], working equations for the calculation of χ and η can be written as:

$$\chi = \frac{I + A}{2} \tag{3}$$

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

Where I and A are the ionization potential and electron affinity, respectively. From the values of the total electronic energy, the ionization potential (I) and electron affinity (A) of the inhibitors are calculated using the following equations:

$$I = E_{(N-1)} - E_N \tag{5}$$

$$A = E_{(N)} - E_{(N+1)} \tag{6}$$

Where $E_{(N-1)}$, $E_{(N)}$, and $E_{(N+1)}$ are the ground state energies of the system with (N−1), (N) and (N+1) electrons, respectively.

During the interaction of the inhibitor molecule with bulk metal, electrons flow from the lower electronegativity molecule to the higher electronegativity metal until the chemical potential becomes equalized. The fraction of the transferred electron, ΔN, was stated through the Eq. (7):

$$\Delta N = \frac{\chi_m - \chi_i}{2(\eta_m + \eta_i)} \tag{7}$$

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