



The effect of structure parameters on the corrosion inhibition effect of some heterocyclic nitrogen organic compounds



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ABSTRACT

The corrosion inhibition effect of pyridine, quinolone, acridine and their *n*-hexadecyl derivatives were studied by quantum chemical methods. The density functional theory (DFT) at the B3LYP/6-311G + (d,p) basis set level, ab initio calculations using the HF/6-311G + (d,p) and semi-empirical PM6 methods were performed to investigate the correlation between its molecular structure and the corresponding corrosion inhibition efficiency (%IE). Inspection of the calculated parameters and corrosion inhibition efficiencies were made to observe any clear links, which might exist between them. Possible correlations between experimental inhibition efficiencies and parameters such as dipole moment (DM), highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals and the differences between them, HOMO–LUMO gap (ΔE), as well as some structural characteristics were investigated. Computational studies have been used to find the most stable adsorption sites for these compounds. This information help to gain further insight about corrosion system, such as the most likely point of attack for corrosion on iron, the most stable site for adsorption and the binding energy of the adsorbed layer

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1. Introduction

The development of corrosion inhibitors based on organic compounds containing nitrogen, sulphur and oxygen atoms are of growing interest in the field of corrosion and industrial chemistries as corrosion poses a serious problem to the iron industry [1,2]. The effect of the molecular structure on the chemical reactivity has been object of great interest in several disciplines of chemistry and quantum-chemistry calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is a useful approach to investigate the mechanisms of reaction in the molecule and its electronic structure level and the structure and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry [3–5]. The geometry of the inhibitor in its ground state, as well as the nature of their molecular orbitals, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are involved in the properties of activity of inhibitors. Pyridine ring system is very widely distributed in nature, especially in plant kingdom. Many important alkaloids atropine from *Atropa belladonna*, Deadly nightshade, contains saturated pyridine nucleus. Many pyridines of commercial interest find application in market areas where bioactivity is important, as in medicinal drugs and in agricultural products such as herbicides, insecticides, fungicides, and plant growth regulators. However, pyridines also have significant market applications outside the

realm of bioactive ingredients. For instance, polymers made from pyridine-containing monomers are generally sold on the basis of their unique physical properties and function, rather than for any bioactivity. Pyridines can be classified as specialty chemicals because of a relatively lower sales volume than commodity chemicals. In ancient times women have used the fluid of leaves of the deadly nightshade to dilate pupils of eyes (mydriatic properties) [6]. The effect of pyridine, quinolone, acridine and their *n*-hexadecyl derivatives on the corrosion rate of mild steel in acid solution has been experimentally studied [7–9]. The aim of this paper is to find a correlation between molecular and electronic structures of the investigated inhibitors and its inhibition efficiency. Molecular orbital calculations were performed looking for good theoretical parameters to characterize the inhibition property of inhibitors, which will be helpful to gain insight into the mechanism of corrosion inhibition and then to simulate the adsorption mode of the inhibitor on the metal surface. Also, we will try to explain which adsorption site is favored to bind the inhibitor to the metal surface.

2. Computational details

2.1. Quantum chemical calculations

Quantum chemical calculations were performed on the corrosion inhibitors. The molecular structures of the investigated compounds were optimized initially with PM6 semiempirical method so as to speed up the calculations. The resulting optimized structures were fully re-optimized using density functional theory (DFT) [10], with the B3LYP hybrid functional, which is a combination of Becke's three parameters (B3)

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exchange functional [11] with the Lee, Yang, and Parr (LYP) correlation functional [12], and the B3LYP/6-311G + (d,p) basis set. Then ab initio Hartree-Fock method (HF), that is the most common type of ab initio calculations, using 6-311G + (d,p) basis set [13]. The structures were drawn using Gauss View, 5.0 implemented in Gaussian 09 package [14]. The corresponding geometries were optimized without any geometry constraints for full geometry optimization. Frequency calculations were executed simultaneously and no imaginary frequency was found indicating a minimal energy structure. According to Koopman's theorem [15], the E_{HOMO} and E_{LUMO} of the inhibitor molecule are related to the ionization potential, I , and the electron affinity A , respectively, by the following relations:

$$I = -E_{\text{HOMO}} \quad A = -E_{\text{LUMO}} \quad (1)$$

Absolute electro negativity, X , and absolute hardness, η , of the inhibitor molecule are given by [16]:

$$X = \frac{(I + A)}{2} \quad \eta = \frac{(I - A)}{2} \quad (2)$$

Softness (σ) is a property of molecule that measures the extent of chemical reactivity. It is defined as the reciprocal of hardness (η). Chemical potential can be expressed as: $\mu = -\chi$. Parr et al. [17] proposed the global electrophilicity power of a ligand as: $\omega = \mu^2/2\eta$. This index measures the stabilization in energy when the system acquired an additional electronic charge from the environment. Electrophilicity encompasses both the ability of an electrophile to acquire additional electronic charge and the resistance of the system to exchange electronic charge with the environment. It contains information about both electron transfer (chemical potential) and stability (hardness) and it is a better descriptor of global chemical reactivity. The obtained values of "X" and " η " were used to calculate the fraction of electron transferred, ΔN , from the inhibitor to the metal surface as follows [18]:

$$\Delta N = \frac{X_{\text{fe}} - X_{\text{inh}}}{2(\eta_{\text{fe}} + \eta_{\text{inh}})} \quad (3)$$

3. Results and discussions

3.1. Quantum chemical calculations

The inhibition of steel using pyridine, quinolone, acridine and their *n*-hexadecyl derivatives as corrosion inhibitors were investigated experimentally. The classification of these inhibitors according to its inhibition efficiency is:

Pyridine (P) < Quinoline (Q) < Acridine (A) < *n*-Hexadecyl pyridine bromide (HDP) < *n*-Hexadecyl quinoline bromide (HDQ) < *n*-Hexadecyl acridine bromide (HDA).

3.1.1. Non-protonated inhibitors

Quantum chemical calculations were performed to investigate the effect of structural parameters on the inhibition efficiency of the inhibitor and study its adsorption mechanism on the metal surface. The geometric and electronic structures of the inhibitors were calculated by the optimization of his bond length, bond angle and dihedral angle. The optimized structure and bond lengths and mulliken charges are shown in Fig. 1.

It was shown from the calculations of the geometrical structure of the investigated compounds that the bond lengths within the ring moiety vary from 1.33 to 1.44 Å in all compounds (conjugated system) and approximately 1.53 Å (sp^3 hybridization) for C—C bond in the aliphatic hydrocarbon chain. The NC bond within the ring moiety has the shortest bond length while C—N aliphatic bond has the longest bond length this probably reflects the weakening of these bonds. The results also showed that the rings are in the same plane of the hydrocarbon chain but it deviated by angle 113.4 in case of *n*-Hexadecyl acridine bromide (HDA).

The inhibition effect of the inhibitor usually depends on the adsorption of those molecules on the metal surface. The adsorption on the metal surface could happen through three modes according to the molecular structures. The first is as neutral molecule via chemisorption mechanism involved sharing of lone pair electron between electronegative atoms and metal. The second is through the intermolecular force, which is relevant to the dipole of the inhibitors. The third is through the plane conjugating system of the aromatic ring, which donate π electrons to the metal surface, accept electrons from the metal surface and the intercalation of hyperconjugating system. The use of Mulliken population analysis to simulate the activation centers for the adsorption of inhibitors on the metal surface has been widely reported and is mostly used for the calculation of the charge distribution over the whole skeleton of the molecule [23]. The more negative the atomic partial charges of the adsorbed center are, the more easily the atom donates its electron to the metal. The calculated Mulliken charges showed that there is more than one active center for each inhibitor. Notably, it was found that, the negative charge is mostly localized on the ring moiety and also on carbon atoms of the aliphatic hydrocarbon chain. This suggests that the binding of inhibitor to the metal surface is through the ring moiety and the aliphatic hydrocarbon chain that are considered as very active centers by which inhibitor compounds could adsorb on the meal surface and so *N*-substituted compounds more inhibition efficiency than the others. The

2.2. Monte Carlo simulations

Monte Carlo simulation studies were performed using Materials studio 4.3 software from Accelrys Inc, which has been used to build inhibitors molecules and Fe surface (as steel) using the sketching tools in Materials Visualizer. [19]. As the three kinds of Fe surfaces (1 1 0, 1 0 0, 1 1 1), Fe (1 1 1) and Fe (1 0 0) surfaces have relatively open structures while Fe (1 1 0) is a density packed surface and has the most stabilization [20]. So we choose Fe (1 1 1) surface as an example from relatively open structures and Fe (1 1 0) surface as the most stable surface to simulate the adsorption process. COMPASS (Condensed Phase Optimized Molecular Potentials for Atomistic Simulation Studies) [21] which is the first ab initio force field that enables accurate and simultaneous prediction of chemical properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of state, cohesive energies, etc.) for a broad range of chemical systems was used to prepare a model of molecules that will adsorb on the surface using Forcite geometry optimization (i.e. Energy minimized). The MD simulation of the interaction between the inhibitor molecules and the Fe surfaces were done by adsorption locator module [22] in a simulation box ($22.90 \text{ \AA} \times 57.26 \text{ \AA} \times 26.68 \text{ \AA}$) with periodic boundary conditions to model a representative part of an interface devoid of any arbitrary boundary effects. The box consists of a Fe slab of 6.00 Å and a vacuum layer of 15.00 Å heights. The interaction energy $E_{\text{Fe-inhibitor}}$ of the steel surface with the inhibitor was calculated according to the following equation:

$$E_{\text{Fe-inhibitor}} = E_{\text{complex}} - (E_{\text{Fe}} + E_{\text{inhibitor}}) \quad (4)$$

where E_{complex} being the total energy of Fe crystal together with the adsorbed inhibitor molecule. E_{Fe} and $E_{\text{inhibitor}}$ being the total energy of Fe crystal and free inhibitor molecules, respectively.

The binding energy was the negative sign value of interaction energy,

$$E_{\text{binding}} = -E_{\text{Fe-inhibitor}} \quad (5)$$

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