



Theoretical evaluation of corrosion inhibition performance of some pyrazine derivatives



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ABSTRACT

The adsorption properties of three pyrazine compounds namely, 2-methylpyrazine (MP), 2-aminopyrazine (AP) and 2-amino-5-bromopyrazine (ABP), for steel corrosion was investigated by quantum chemical calculation and quenched force-field molecular dynamics simulation. Global reactivity parameters such as E_{HOMO} , E_{LUMO} , the energy gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$), dipole moment, have been calculated and discussed. Fukui indices were calculated to describe the local reactive sites of the molecules. The equilibrium adsorption behaviour of these pyrazine molecules on Fe (110) surface was investigated using molecular dynamics simulation. The binding energy followed the order: $\text{ABP} > \text{AP} > \text{MP}$, which is in agreement with experimental results.

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1. Introduction

An important method of protecting metallic materials against deterioration due to corrosion is by the use of organic inhibitors. But a major impediment in designing new corrosion inhibitors is that the mechanism by which these chemical compounds (inhibitors) prevent the corrosion of metals and alloys is not well understood [1]. The importance of determining the mechanism is illustrated by the strong dependence of inhibition efficiency upon minor changes in the chemical structure of these compounds [2]. Experimental evidence in support of specific mechanisms has been difficult to obtain due to the following reasons: (i) the low concentrations at which these inhibitors are used (a few ppm), (ii) the complexity of the environments surrounding the inhibitor under real conditions (water at high ionic strengths), and (iii) the difficulty in experimentally obtaining atomistic information about the metal/inhibitor interface.

To mitigate the above problems, the use of quantum chemical calculations supported by the molecular dynamics simulations can be effective in elucidating the mechanism of inhibition of corrosion inhibitors on metal surfaces at the molecular level. This methodology is widely reported as a very useful tool in corrosion inhibitor design [3–10]. For instance, the inhibition performance of four 1-R-2-undecyl-imidazoline compounds ($\text{R} = \text{CH}_2\text{COOH}$, $\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_2\text{CH}_2\text{NH}_2$ and H) with different hydrophilic groups using quantum chemistry and molecular dynamics simulations

was investigated theoretically by Zhang et al. [11]. The results obtained indicate that the hydrophilic groups (R) have a remarkable influence on molecular reactivity and binding strength between the inhibitor molecules and the Fe surface. In our previous communications, we investigated the correlation between the results of quantum chemical calculations and the experimental corrosion inhibition efficiencies of benzimidazole derivatives [12], xanthene and its derivatives [13], quinoline derivatives [14], triazoles and benzimidazole derivatives [15] and phenanthroline derivatives [16]. Results obtained in these studies have shed more light into the reactivity, active sites and the mechanism of interaction of these inhibitors with steel surface. The use of computational chemistry methods as a tool in investigating the mechanism of corrosion inhibition will continue to make great impact in corrosion science research in the future because of the ongoing computer hardware and software advances [17,18]. Recently, there is a substantive effort in the literature especially on the use of Density Functional Theory (DFT) as a powerful theoretical tool in analyzing inhibitor/surface interaction [19–24].

The aim of the present work is to bridge the gap in information by providing quantum chemical and molecular dynamics results using models utilizing computational chemistry approaches and techniques in order to provide theoretical insights on the mechanism of inhibition action of 2-methylpyrazine (MP), 2-aminopyrazine (AP) and 2-amino-5-bromopyrazine (ABP) recently reported as a good corrosion inhibitors for steel in acidic medium [25]. This information will be useful towards a rational design of corrosion inhibitors based on pyrazine moiety, since literature reports on the use of pyrazine derivatives as corrosion inhibitors are scarce [26,27].

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2. Computational details

2.1. Quantum chemical calculations

Density Functional Theory (DFT) is certainly the most widely applied ab initio approach for modelling the ground-state (GS) properties of molecules, clusters and solids. Interestingly this model was originally viewed as unable to describe chemical bonds, but continuous improvements of the exchange–correlation functionals – the only approximated term in DFT, has allowed DFT to become a blockbuster in both chemistry and physics [28]. In the present work, DFT calculations was carried out using the Gaussian-03 program [29]. The exchange–correlation was treated using hybrid, B3LYP functionals. A full optimization was performed using the 6-311G++(d,p) basis sets. This basis set is well known to provide accurate geometries and electronic properties for a wide range of organic compounds [30]. Moreover, 6-311G++(d,p) basis set was used because it gives, according to convergency tests, results comparable to those obtained from plane-wave calculations; the differences in energies and bond lengths between the 6-311G++(d,p) and plane-wave basis sets are ~0.01 eV and <0.01 Å, respectively [30]. A vibrational analysis was carried out for each optimized molecule to ensure that they are in a minimum (no imaginary frequency). It is well known that the phenomenon of electrochemical corrosion takes place in aqueous phase. Therefore, in order to ensure the accuracy of the data, solvent effect has to be taken into account in the calculation. In this study, SCRf methods (Self-Consistent Reaction Field) were performed, using the polarized continuum method (PCM) as a model for solvent. In this model, the solvent is treated as an expanse of dielectric media and the solute as a trapped molecule in a cavity surrounded by the solvent [31]. All calculations were conducted in aqueous phase. The condensed Fukui function calculations were performed with Material Studio Dmol³ 6.0, using a double-numerical with polarization (DNP) basis set in combination with generalized gradient approximation (GGA) and BLYP exchange–correlation functionals. Hirshfeld population analysis was used for the presentation of Fukui function.

Within the framework of the density functional theory, the chemical potential (μ) is defined as the negative of electronegativity (χ) [32]:

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

and hardness (η) is defined as [33]:

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

Using the finite difference approximation, global hardness and chemical potential can be approximated as [34]:

$$\eta = \left(\frac{I - A}{2}\right) \quad (3)$$

$$\mu = -\left(\frac{I + A}{2}\right) \quad (4)$$

where I and A are the first vertical ionization potential and electron affinity, respectively, of the chemical system.

Using Koopmans theorem [35], and by setting $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$, chemical potential and global hardness can be expressed as:

$$\mu = \frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \quad (5)$$

and

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \quad (6)$$

where E_{HOMO} is the energy of highest occupied molecular orbital and E_{LUMO} is the energy of the lowest unoccupied molecular orbital.

The global softness (S), is the inverse of global hardness and is given as [36]:

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \quad (7)$$

The global electrophilicity index (ω) was introduced by Yang and Parr [37] and is given by:

$$\omega = \frac{\mu^2}{4\eta} \quad (8)$$

The Fukui function which measures reactivity in a local sense, is by far the most important local reactivity index [38]. Using a scheme of finite difference approximations, this procedure condenses the values around each atomic site into a single value that characterizes the atom in the molecule. With this approximation, the condensed Fukui function becomes:

$$f_k^+ = q_k(N + 1) - q_k(N) \quad (\text{for nucleophilic attack}) \quad (9a)$$

$$f_k^- = q_k(N) - q_k(N - 1) \quad (\text{for electrophilic attack}) \quad (9b)$$

where $q_k(N + 1)$, $q_k(N)$, and $q_k(N - 1)$ are charge values of atom k for cation, neutral and anion, respectively.

2.2. Molecular dynamics simulations

MD simulations of the interaction between inhibitor molecules and the Fe surface were carried out using Materials Studio 6.0 (from Accelrys Inc.) [39,40]. To construct the interaction model, the Fe cell was first optimized, followed by a four-step model construction which include: (i) cleaving the surface along (110) plane and relaxing the surface; (ii) building the 2D surface into a super cell (12×10) containing the Fe surface in a simulation box of $29.78 \times 24.82 \times 28.18$ Å; (iii) adding a vacuum slab above the Fe to build a 3D cell, and setting the vacuum thickness as 30 Å; (iv) placing the energy minimized inhibitor molecules onto a proper position of the Fe surface and ensuring the whole molecule is inside the vacuum slab.

After constructing the 3D interaction models, dynamics simulations were performed using the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field and the String Matching Algorithms Research Tool (smart algorithm). COMPASS 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. It is also the first high quality force field to consolidate parameters of organic and inorganic materials. The system was equilibrated in NVT ensemble (i.e. canonical ensemble) at 298.0 K with a time step of 0.1 fs and a simulation time of 50 ps using the Nose thermostat. The system was quenched every 500 steps with convergence tolerance energy at 1.0^{-3} kcal/mol.

Interaction energies between Fe surface and inhibitor molecules was then estimated using single point energy calculation as follows [8]:

$$E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhibitor}}) \quad (10)$$

where E_{total} is the total energy of the surface and inhibitor, E_{surface} , the surface energy, $E_{\text{inhibitor}}$ is the energy of inhibitor molecule. The binding energy was computed as $E_{\text{binding}} = -E_{\text{interaction}}$. Solvent and charge effects were ignored in all simulations and calculations were performed at the metal/vacuum interface. Although this method clearly oversimplifies the factual situation, it is adequate and has been used by many researchers to illustrate the differences

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