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A comparative density functional theory and molecular dynamics simulation studies of the corrosion inhibitory action of two novel N-heterocyclic organic compounds along with a few others over steel surface

Sourav Kr. Saha [a,b], Abhiram Hens [b,c], Naresh Chandra Murmu [a,b], Priyabrata Banerjee [a,b,*]

[a] Surface Engineering & Tribology Group, CSIR-Central Mechanical Engineering Research Institute, Mahatma Gandhi Avenue, Durgapur 713209, West Bengal, India
[b] Academy of Scientific and Innovative Research (AcSIR), CSIR-CMERI Campus, Durgapur 713209, West Bengal, India
[c] Micro System Technology Group, CSIR-Central Mechanical Engineering Research Institute, Mahatma Gandhi Avenue, Durgapur 713209, West Bengal, India

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ABSTRACT

Four novel pyrazine derivatives namely 2-aminopyrazine (AP), 2-amino-5-bromopyrazine (ABP), 3-amino pyrazine-2-thiol (APT) and 3-amino-6-bromopyrazine-2-thiol (ABPT) are investigated for their possible utilization as corrosion inhibitors by computational chemistry using density functional theory (DFT) and molecular dynamics (MD) simulation. Organic molecules (AP and ABP) along with two other similar organic framework (APT and ABPT) having an additional –SH group have been thoroughly investigated as corrosion inhibitors by means of theoretical investigation (DFT and MD simulation) with a vision that they can perform better. Their corrosion inhibition property have been calculated by several energy parameters like E_{HOMO}, E_{LUMO}, energy gap (ΔE), electronegativity (χ), softness (S) and fraction of electron transferred from inhibitor molecule to metallic atom (ΔN). Local reactivity of these molecules has been studied through Fukui indices. Significantly, DFT and MD simulation results are in well agreement with experimental outcomes for AP and ABP. Moreover the theoretical results show that –SH based pyrazine derivatives *i.e.*; APT and ABPT, are even better potential candidate as corrosion resistant. Theoretical outcome reflects that introduction of –SH group will result betterment towards inhibition property.

1. Introduction

Corrosion inhibition of metal surfaces is a long standing area of research due to its industrial significance. Among numerous corrosion inhibition initiatives, selections of organic molecules as inhibitors are widely acclaimed in view of their economic advantage, higher efficiency and technological feasibility. Organic inhibitors are used in acid solutions for protection of metal surfaces from corrosion by forming a film on the metal surface. Several organic heterocyclic compounds with various hetero atoms as well as several pi-bonds are promising corrosion inhibitors [1–5]. Corrosion inhibition in acid solutions depends on the physico-chemical interaction between metal surface and concerned inhibitor molecules. The organic heterocyclic compound should have active donor sites which are capable of forming coordination bonds with metallic surfaces [6,7]. It is noteworthy that with organic heterocyclic compound, the coordinate bonds are stronger, which is also reflected in their better inhibition properties. After several research works it have been concluded that inhibition efficiency is associated with molecular structure, chemical composition, molecular electronic distribution, surface charge density and their affinity to metal surfaces [8,9]. In this regards several molecules have been synthesized and explored their inhibition proficiencies. Among several molecules, heterocyclic organic compounds *e.g.*; pyrazine and its substituted derivatives have prospects of showing remarkable corrosion resistance property in acid media [10,11]. Depending on availability of lone pair of electrons on organic heterocyclic compound and based on metal-heteroatom interactions, several pyrazine derivatives have the prosperity to enact as efficient corrosion-inhibitors. In its continuation, in this end, it becomes obligatory to counter explore the theoretical modelling for two pyrazine derivatives (*e.g.*; 2-aminopyrazine (AP) and 2-amino-5-bromopyrazine (ABP)) as corrosion inhibitors on steel surface in acidic aqueous medium [12]; which furthermore instigates for additional exploration of hitherto unexplored pyrazine derivatives such as 3-amino pyrazine-2-thiol (APT) and 3-amino-6-bromopyrazine-2-thiol (ABPT) which seems to have better prospect and potential to become a good corrosion inhibitor.

* Corresponding author at: Surface Engineering & Tribology Group, CSIR-Central Mechanical Engineering Research Institute, Mahatma Gandhi Avenue, Durgapur 713209, West Bengal, India.
E-mail address: pr_banerjee@cmeri.res.in (P. Banerjee).

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Traditional methods for developing inhibitors are based on small to large-scale wet chemical experimentations, which involves time and cost in sufficient extent. In recent times, density functional theory (DFT) and molecular dynamics (MD) based computational studies have emerged as an alternative way of evaluation for a wide range of physico-chemical properties of several molecules. Advancement of this computational experimentation has certainly reduced the time and cost associated with rigorous experimentation. It is found that such quantum chemical and classical MD based studies of corrosion inhibition mechanism over organic heterocyclic molecules are scarce in literature [13–16]. Especially, newly designed organic inhibitors *e.g.*; pyrazine derivatives (APT and ABPT), have not been explored till date.

The very aim of this present work is to carry out a detail computational investigation of the inhibition mechanism of a few selective pyrazine derivatives. For this, DFT based quantum chemical calculation and classical MD simulations are performed and finally the outcomes are compared with the available experimental results of surveyed literature [12]. Such analysis reveals that hitherto less explored pyrazine derivatives such as APT and ABPT could be potentially used as promising corrosion inhibitors. The complete theoretical investigation is well supported by calculation of relevant molecular properties of inhibitors followed by explanation of the mechanism of inhibition on steel surface. The relative inhibition efficiency is calculated by quantum chemical indices: E_{HOMO}, E_{LUMO}, energy gap (ΔE), electronegativity (χ), softness (S) and fractions of transferred electrons from the inhibitor to the metallic surface (ΔN). MD simulations are also carried out to explore inhibitor interaction with Fe (1 1 0) surface.

2. Methodology

2.1. Computational details for quantum chemical calculation

In this present study, geometry optimization and several quantum chemical parameters of the studied inhibitor molecules are obtained by DFT calculations using the ORCA programme module (version 2.7.0) [17] which is an open source code developed by Prof. Dr. Frank Neese (Director, MPI für Chemische Energiekonversion, Muelheim, Germany). DFT is a most widely accepted *ab initio* approach for modelling ground states of molecules. Geometry optimizations and exchange correlations are treated using hybrid B3LYP [18–23] and full optimization was performed with SVP/SV(J) basis set [13,14,24], which is well acclaimed to provide accurate geometry and electronic properties for molecules within a wide range. The all-electron Gaussian basis sets were developed by the Ahlrichs group [25]. Herein, triple-ζ quality basis sets TZV(P) with polarization functions on the atoms like N, S, Br *etc.* are considered [26]. For carbon and hydrogen like elements, polarized and smaller split-valence double-ζ quality SV(P) basis sets are used in the valence domain and for non-hydrogen atoms a polarizing set of d functions are used. Self consistent field (SCF) calculations are tightly converged (1×10^{-8} Eh in energy, 1×10^{-7} Eh in the density change, and 1×10^{-7} in maximum element of the DIIS error vector). All the theoretical parameters are calculated in the solution phase because it is well known that the electrochemical corrosion always happen in solution phase. As a result, it was necessary to incorporate the solvent effect in the computational calculations. Here, COSMO model was applied in order to incorporate the effect of solvent (here, water) in this calculation [16]. Conductor like screening model (abbreviated as COSMO) is an efficient and elegant way to calculate the energies, structures and properties of molecules in solution. The solvent is represented as a dielectric polarizable continuum. In the COSMO approach it is initially assumed to be a perfect conductor which completely shields ('screens') the charge density of the solute. This method here models solvent molecules as a continuum of uniform dielectric constant (ε) and herein solute is consigned as a uniform series of inlocking atomic spheres.

The local reactivity has been analysed by evaluating Fukui indices (FI). The FI calculation has been performed using Dmol^3 module of Material studio™ version 6.1 by Accelrys Inc., San Diego, CA [27]. All the calculations have been performed using B3LYP like exchange correlation functional and double numerical with polarization (DNP) basis set, because this set is the best set available in Dmol^3 [28]. Fukui indices are used to obtain local reactivity information [29]. The Fukui function f_k is described as a first derivative of the electronic density $\rho(\vec{r})$with respect to the number of electrons (N) in a constant external potential $\upsilon(\vec{r})$ [30].

$$f_k = \left(\frac{\partial\rho\left(\vec{r}\right)}{\partial N}\right)_{\upsilon\left(\vec{r}\right)} \tag{1}$$

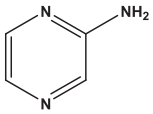
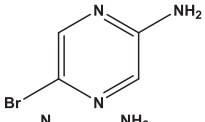
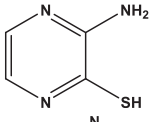
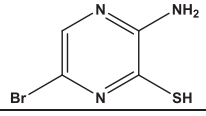
The Fukui functions can be expressed as [31]:

$$f_k^+ = q_k(N+1) - q_k(N) \quad \text{(for nucleophilic attack)} \tag{2}$$

$$f_k^- = q_k(N) - q_k(N-1) \quad \text{(for electrophilic attack)} \tag{3}$$

where gross charge of k atom is denoted by q_k (in space electronic density at point r around the molecule). The q_k $(N + 1)$, q_k (N) and

Table 1
IUPAC name, molecular structure, abbreviation and molar mass of the studied molecules.

Inhibitors	Structure	Abbreviation	Molar mass (g/mol)
2-aminopyrazine		AP	95.1
2-amino-5-bromopyrazine		ABP	174
3-aminopyrazine-2-thiol		APT	113.16
3-amino-6-bromopyrazine-2-thiol		ABPT	206.06