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Density functional theory and molecular dynamics simulation study on corrosion inhibition performance of mild steel by mercapto-quinoline Schiff base corrosion inhibitor

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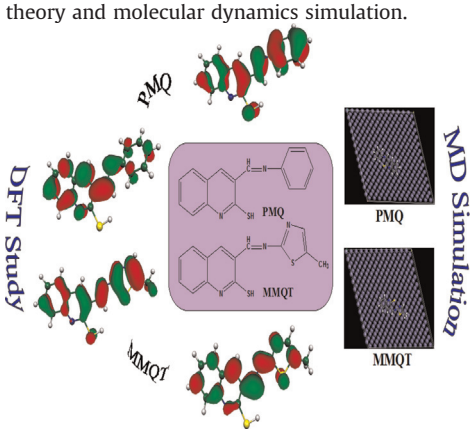
HIGHLIGHTS

- Performance of two mercapto-quinoline Schiff base as corrosion inhibitor was investigated theoretically.
- Quantum chemical calculations and molecular dynamics simulation were performed.
- Fukui indices have been used to analyze the local reactivity of the studied inhibitors.
- Theoretical calculations agree well with the experimental findings.

GRAPHICAL ABSTRACT

Corrosion inhibition performances of two mercapto-quinoline Schiff base inhibitors have been performed and have correlated their experimentally observed inhibition efficiency by density functional theory and molecular dynamics simulation.



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ABSTRACT

Corrosion inhibition mechanism of two mercapto-quinoline Schiff bases, *eg.*, 3-((phenylimino)methyl) quinoline-2-thiol (PMQ) and 3-((5-methylthiazol-2-ylimino)methyl) quinoline-2-thiol (MMQT) on mild steel surface is investigated by quantum chemical calculation and molecular dynamics simulation. Quantum chemical parameters such as E_{HOMO}, E_{LUMO}, energy gap (ΔE), dipolemoment (μ), electronegativity (χ), global hardness (η) and fraction of electron transfers from the inhibitor molecule to the metallic atom surface (ΔN) have been studied to investigate their relative corrosion inhibition performance. Parameters like local reactive sites of the present molecule have been analyzed through Fukui indices. Moreover, adsorption behavior of the inhibitor molecules on Fe (1 1 0) surface have been analyzed using molecular dynamics simulation. The binding strength of the concerned inhibitor molecules on mild steel surface follows the order MMQT > PMQ, which is in good agreement with the experimentally determined inhibition efficiencies. In view of the above, our approach will be helpful for quick

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Quantum chemical calculations
Molecular dynamics simulation

prediction of a potential inhibitor from a lot of similar inhibitors and subsequently in their rational designed synthesis for corrosion inhibition application following a wet chemical synthetic route.

1. Introduction

Nowadays use of acid solutions in numerous industrial techniques such as acid pickling, acid cleaning, oil acidification, petrochemical industries, *etc.* are very common [1–3]. Those acid solutions result in serious metallic corrosion further resulting in a huge economic loss. Among several widely used methods, the most effective and economic method is to dissolve inhibitors in acid solutions to prevent the metallic corrosion [4,5]. Nature is changing in a drastic way and keeping this in mind, shielding of metal surface from corrosion is a commendable job in the field of material science. In this context, development of low cost and easy-to-make organic inhibitors is highly demanding from industrial point of view. In this field, the experimental fact obtained from several researchers have pointed out that organic compounds containing nitrogen, oxygen and sulphur-like hetero-atoms show better inhibition efficiency in different destructive media [6,7]. In general, inhibitor molecules adsorb on the metallic surface following a physical or chemical adsorption route and eventually a protective layer is formed [8–10]. Physical adsorption is regarded as electrostatic interactions between the inhibitor molecules and metallic surface whereas chemical adsorption happens by the charge sharing or transfers from the inhibitor molecules to the metallic surface [11].The efficiency of the inhibitor molecule on metallic surfaces is directly proportional to the strength of the newly formed bonds. Inhibitors having N, O and S donor sites, unsaturated bonds along with planar conjugated aromatic moieties are preferred as good corrosion inhibitors, considering their capability to donate available lone pair of electrons or acceptance of electrons in empty low-lying d-orbital of metals [12–14]. Traditionally, weight loss, polarization curves, electrochemical impedance spectroscopy are main routes for testing inhibition performance; however, these are all high cost, time consuming microcosmic inhibition processes [15,16]. In view of the above, quantum chemical and molecular dynamics simulation is the most authentic technique which has enormous advantages of evaluating microcosmic inhibition performance and exploration of their mechanism well in advance.

Among the available computer simulation methods, determination of geometry optimized electronic structure as well as mechanism of inhibition of the so-called organic inhibitor molecules can be successfully elucidated by quantum chemical calculations [17–21]. Recently, substantiate attempt is found in the literature for the use of quantum chemical calculation as an influential theoretical tool to analyze surface-inhibitor interactions [21]. In general, frontier molecular orbital energy, fraction of electron transfer from inhibitor molecule to metallic surface, dipole moment and global hardness are considered as parameters to obtain the inhibition performance of organic inhibitor molecules in many cases [22,23]. However, Kokali et al. have proposed that only quantum chemical calculation is not sufficient enough to envisage the trend of inhibitive performance of corrosion inhibitors [24–26]. In many cases, computed outcomes obtained from quantum chemical calculations cannot be correlated with the proper experimental findings [27,28]. Therefore, a precise modeling of experiments should be emphasized for visualizing the interaction of inhibitor molecules with metal surfaces. This modeling will help to correlate the theoretical and experimental findings in an improved manner. Quantum chemistry calculations are usually accurate in terms of total electron calculation, while disadvantages are their huge work load execution and being time-consuming too. In real practice, sometimes it is difficult to deal with any large system having hundreds or thousands of atoms. Henceforth, compared to quantum chemistry, molecular dynamics are obviously better choices keeping it in mind that only atom – atom interaction is calculated whereas in no way electron–electron interactions are considered. Molecular dynamics (MD) simulation is therefore introduced, which can provide the actual interfacial configuration and adsorption energy of the surface adsorbed inhibitor molecules [29,30]. Till date a few groups are only working on it to understand the interaction mechanism of inhibitor molecules with the metallic surface. Xia et al. recently studied the relationship between structural conformation of imidazoline derivatives and their inhibition efficiencies by applying MD simulation [31]. Yang et al. have also employed this sophisticated tool to study the adsorption behavior of thiosemicarbazone type inhibitor molecules on mild steel surface [32].

As a part of our ongoing research, we have studied both quantum chemical calculation and MD simulation to correlate the theoretical results with experimental outcomes [33,34]. The aim of this present work is to find out an alternative approach to correlate the corrosion inhibition performance of an inhibitor on a metal surface without doing any wet chemical experimentation, which obviously deserves certain importance from economic point of view. Our first and foremost duty will be to correlate the theoretical results with recently available literature reports on experimental findings. Keeping it in mind, we have executed both quantum chemical calculation and MD simulation on the recently studied selective heterocyclic inhibitor molecules, namely, 3-((phenylimino)methyl)quinoline-2-thiol (PMQ) and 3-((5-methylthiazol-2-ylimino)methyl)quinoline-2-thiol (MMQT) over a steel surface in acidic media [35]. The results obtained from theoretical studies are in good accordance with experimental outcomes. In this perspective, for finding out promising unexplored corrosion inhibitors, before doing hard core synthetic and wet chemical experimentation or any other expensive experimental studies we may check their efficacy as a corrosion inhibitor by simple theoretical experimentation. These findings must be helpful for rational designing of a promising corrosion inhibitor. However, till date literature survey has revealed that instances of analogous studies of a complete agreement of experimental results with theoretical outcomes are relatively less [36].

2. Computational details

2.1. Quantum chemical calculation

Geometry optimization and various quantum chemical parameters are obtained by density functional theory (DFT) calculations using the ORCA program package (ORCA is a highly flexible, efficient and easy-to-use general purpose tool for quantum chemistry; version 2.7.0) [37]. DFT is a most widely accepted ab initio approach for modeling ground states of molecules. Geometry optimizations and exchange correlations are treated using hybrid B3LYP [38–41] and full optimization is performed with SVP/SV(J) basis set, which is well accepted to provide accurate geometry and electronic properties of molecules. The all-electron Gaussian basis sets are developed by the Ahlrichs group [42]. In this calculation, triple-ζ quality basis sets TZV(P) with one set of