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COMPUTATIONAL ELECTROCHEMISTRY TECHNIQUES USED IN CORROSION INHIBITION STUDIES

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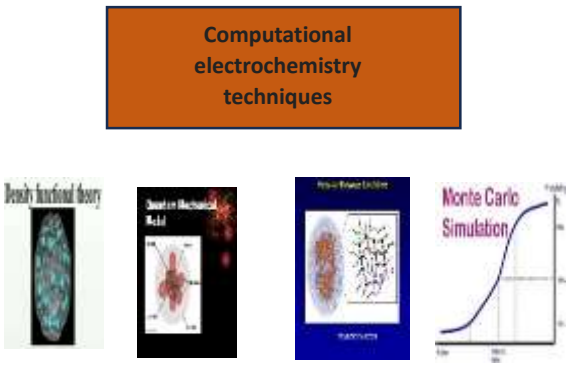
Abstract: In many sectors, corrosion is a major issue with serious economic and safety ramifications. To reduce material deterioration and maintain the durability of structures and equipment, efficient corrosion inhibitors must be developed. Computational electrochemistry techniques have become effective resources for comprehending corrosion mechanisms and creating new inhibitors in recent years. This article gives a general overview of the computational methods used in corrosion inhibition research, including Quantum Mechanics/Molecular Mechanics (QM/MM), Molecular Dynamics (MD), and Density Functional Theory (DFT) simulations. Despite the various benefits, computational electrochemistry methods have several drawbacks, such as the necessity for precise modeling of complicated systems and the high computer resource requirements. To close the gap between atomistic simulations and macroscopic behavior, future efforts should concentrate on increasing precision, broadening the scope of simulations, and using multi-scale modeling techniques. By shedding light on the mechanisms underlying corrosion and assisting in the creation of effective inhibitors, computational electrochemistry approaches have transformed the study of corrosion inhibition. With these methods, it is possible to find innovative corrosion inhibitors with improved performance and hasten the development of corrosion protection systems.



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Introduction

Corrosion is an electrochemical process that occurs when metals or alloys react with their surrounding environment, resulting in the gradual deterioration and degradation of the material (Perez, 2016). The process involves the transfer of electrons from the metal to the environment, leading to the oxidation of the metal and its eventual dissolution. The phenomenon is widespread and affects various industries, including infrastructure, transportation, oil and gas, manufacturing, and marine sectors. corrosion is a common and expensive issue that impacts many different businesses. Corrosion inhibition is the process of reducing or preventing corrosion on metallic surfaces by using chemical or electrochemical compounds. Corrosion inhibitors work by forming a protective layer on the surface of the metal that prevents corrosive agents from reaching the metal surface. Corrosion inhibitors are important in mitigating corrosion because they can help to extend the lifespan of metallic components and reduce financial losses (Jellesen, 2018). The creation of powerful corrosion inhibitors is essential for preventing corrosion and extending the lifespan of metallic components. Traditional empirical methods for designing and evaluating inhibitors can be time- and resource-consuming, and they have some limitations in terms of their capacity to provide a thorough knowledge of the underlying electrochemical processes (Jellesen, 2018). Computational electrochemistry approaches have become effective resources for researching corrosion mechanisms and creating new inhibitors in recent years. Utilizing the capability of computational modeling and simulation, computational electrochemistry approaches offer insights into the interactions of inhibitors and metal surfaces at the atomic and molecular levels. The calculation of the electronic structures, energies, and reactivity of corrosion inhibitors is made possible by density functional theory (DFT), offering important insights into their stability, adsorption behavior, and inhibitive capabilities. Researchers can examine the dynamic behavior of inhibitors on metal surfaces, including their adsorption, diffusion, and interaction mechanisms, using molecular dynamics (MD) simulations (Atar *et al.*, 2021). Understanding the mechanics of corrosion inhibition is aided by Monte Carlo (MC) simulations, which offer statistical insights into the adsorption behavior and coverage of inhibitors on metal surfaces. In order to examine inhibitor-metal surface interactions with great accuracy and detail, quantum mechanics/molecular mechanics (QM/MM) simulations combine quantum mechanical calculations with molecular mechanics methods. The design and optimization of corrosion inhibitors can be sped up by using these computational methodologies, which also lessens the reliance on empirical trial-and-error techniques. Computer simulations can be used to forecast inhibitor performance, evaluate how well they work in various environments, and

direct the production of new compounds with enhanced inhibitory qualities. Additionally, computational electrochemistry methods enable a greater comprehension of the fundamental mechanisms governing corrosion inhibition, delivering knowledge that can guide the creation of more precise and effective inhibitor tactics (Al-Amiery *et al.,* 2022). The aim of this article is to provide a thorough knowledge of the underlying electrochemical processes and the following techniques are discussed which include Quantum Mechanics/Molecular Mechanics (QM/MM) simulations, Molecular Dynamics (MD) simulations, Monte Carlo (MC) simulations, and Density Functional Theory (DFT) simulations, which provide a deeper understanding of the intricate electrochemical processes involved in corrosion and their inhibition.

Computational electrochemistry techniques used corrosion inhibition

Density Functional Theory (DFT)

In the field of materials science, including research on corrosion inhibition, density functional theory (DFT) is a popular computational technique. Based on quantum mechanics, it offers a useful method for describing the electrical structure and characteristics of materials, such as the interactions between inhibitors and metal surfaces. The electron density, which explains how electrons are distributed in a system, is a key notion in the DFT theory. The Hohenberg-Kohn theorems indicate that the electronic energy of a system is solely determined by the ground-state electron density. To calculate the electronic characteristics and reactivity, DFT expresses the system's energy as a function of the electron density (Sahni, 2004).

Density functional theory (DFT) has numerous applications in corrosion inhibition studies:

i. Calculation of Electronic Structures: DFT allows the calculation of electronic structures, including the distribution of energy levels and orbital properties. By analyzing the electronic structure of inhibitors, researchers can gain insights into their electronic properties, such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which are essential for understanding their reactivity and potential as corrosion inhibitors (Parul, *et al.,* 2017).

ii. Evaluation of Adsorption Energies: DFT can determine the adsorption energies of inhibitors on metal surfaces, which is crucial for assessing their affinity and stability. By calculating the adsorption energies, researchers can predict the strength of the inhibitor-metal interaction, providing insights into the inhibitor's ability to adhere to the metal surface and inhibit corrosion.

iii. Prediction of Reaction Barriers: DFT can be used to calculate activation energies and reaction barriers involved in corrosion processes. By studying the energy barriers associated with corrosion reactions, researchers can identify the steps that are most likely to be inhibited by the presence of an inhibitor. This information aids in understanding the inhibitory mechanism and designing inhibitors with optimal reactivity (Ebrahimi, *et al.,* 2021)

iv. Screening of Inhibitor Candidates: DFT enables the screening and evaluation of a large number of inhibitor candidates. By calculating electronic structures, energy levels, and reactivity of various compounds, researchers can prioritize the most promising candidates for further experimental testing, saving time and resources (Parul, *et al.,* 2017).

Additionally, DFT can provide insights into the charge transfer processes between the inhibitor and metal surface, the nature of chemical bonding, and the influence of environmental factors on inhibitor effectiveness. DFT is a valuable tool in corrosion inhibition studies as it offers a detailed understanding of the electronic properties and reactivity of inhibitors. By leveraging DFT calculations, researchers can identify and design inhibitors with optimal adsorption energies, reaction barriers, and reactivity, contributing to the development of more effective corrosion protection strategies (Oukhrib, *et al.,* 2021).

Molecular Dynamics (MD) simulations

The behavior and interactions of atoms and molecules over time are studied using computational methods called molecular dynamics (MD) simulations. In the context of investigations on corrosion inhibition, molecular dynamics (MD) simulations provide light on the mechanisms of inhibition by offering insights into the atomic-level dynamics and interactions between inhibitors and metal surfaces. The foundations of MD simulations are found in classical mechanics, where interatomic potential energy functions are used to trace the locations and velocities of atoms as they change over time. MD simulations simulate the paths of atoms and molecules by resolving Newton's equations of motion, enabling real-time observation of their behavior and interactions (Xu, *et al.,* 2022).

In studies on corrosion inhibition, MD simulations have a variety of uses:

i. Understanding Adsorption Mechanisms: MD simulations help clarify how inhibitors bind to metal surfaces and cause adsorption. The initial adsorption, binding orientations, and stability of the inhibitor can all be observed by researchers by modeling the movement and behavior of inhibitor molecules close to the metal surface. This knowledge sheds light on the processes of inhibition and aids in understanding the variables affecting inhibitor adsorption (Huang, *et al.,* 2018).

ii. Investigating Diffusion and Transport: Using MD simulations, it is possible to examine the diffusion and transport of inhibitors on metal surfaces. Researchers can measure the diffusion coefficients, diffusion paths, and residence durations of inhibitor compounds by tracking their movements. Understanding how inhibitors spread and move on the surface requires knowledge of this.

iii. Examining Interactions with Corrosion Sites: Using MD simulations, one may examine how certain corrosion sites, such as active sites or defect sites on the metal surface, interact with inhibitors. Researchers can learn more about the interactions that control the inhibition of corrosion

processes at certain places by observing the activity of inhibitor molecules close to these spots (Huang, *et al.,* 2018).

iv. Examining the Inhibitor-Metal Interface: MD simulations can give you a thorough knowledge of how inhibitors and metal surfaces interact. Researchers can learn more about the elements that affect the stability and adhesion of inhibitors as well as their capacity to effectively control corrosion by examining the interfacial structure, interactions, and characteristics.

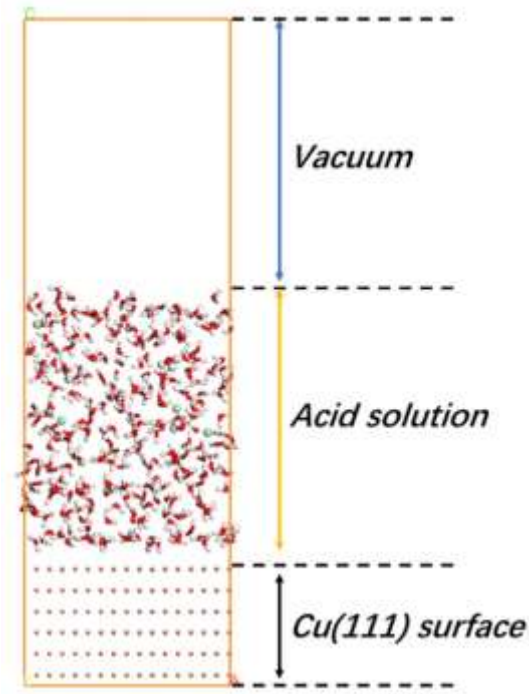

Figure 1.0 Schematic diagram of the MD simulation model Xu, *et al.,* 2022

For instance, MD simulations can show the adsorption modes of the inhibitor on the metal surface, the formation of inhibitor-metal complexes, and the effects of temperature and environment on the stability of the adsorbed inhibitor layer in a study on the inhibition of corrosion of steel by organic compounds (Haris, *et al.,* 2021). These revelations aid in the comprehension of the inhibitory mechanism and offer suggestions for the creation of more effective inhibitors. In a study on the corrosion inhibition of copper in hydrochloric acid solution, molecular dynamics simulations were used to study the corrosion inhibition mechanism of cysteine (Cys), glutamic (Glu) and glycine (Gly). The adsorption energy and radial distribution function results show that all three amino acids can spontaneously adsorb (Xu, *et al.,* 2022). MD simulations offer a useful tool for examining the behavior and interactions of inhibitors at the atomic level. MD simulations provide in-depth insights into the mechanisms of inhibition and aid in the logical design of efficient corrosion inhibitors by modelling the dynamics of inhibitor molecules and their interactions with metal surfaces (Xu, *et al.,* 2022).

Monte Carlo (MC) simulations

Computing methods called Monte Carlo (MC) simulations are used to describe and examine systems having random components. In investigations on corrosion inhibition, MC simulations are used to examine the adsorption and desorption processes of inhibitors on metal surfaces, revealing important details about their interactions and behavior (Chandrabhan, *et al.,* 2018). The basic idea behind MC simulations is to generate random system configurations and assess the thermodynamic probability of each one. As the simulation moves forward, several configurations are iteratively sampled in accordance with predetermined principles, such as the Metropolis algorithm or the Gibbs ensemble approach. A probability is given to each configuration depending on its energy or other pertinent characteristics. To calculate adsorption and desorption probabilities as well as other thermodynamic parameters, statistical averages can be obtained by sampling a lot of setups (Cooley, J. & Evans, M. 2005).

Applications for MC simulations in research on corrosion inhibition include the following:

i. Adsorption Behavior: The adsorption of inhibitors on metal surfaces can be modeled using MC simulations. Researchers can calculate the adsorption probabilities and quantify the coverage of inhibitors on the surface by modelling the random adsorption process. This information sheds light on the spatial arrangement and distribution of inhibitors, enabling a better understanding of how efficient they are at obstructing active sites and lowering corrosion rates (Chandrabhan, *et al.,* 2018).

ii. Processes involved in desorption: MC simulations can also simulate the removal of inhibitors from metal surfaces. Researchers can assess desorption rates and investigate the stability of the inhibitor layer by taking the likelihood of inhibitor molecules leaving the surface into account. Understanding the persistence and long-term effectiveness of inhibitors requires knowledge of this information.

iii. Competing Adsorption: MC simulations can examine the conflict for adsorption sites on the metal surface between inhibitors and other substances. Researchers can assess the preferred adsorption and displacement behavior by modelling the random adsorption of several species. This reveals information on the efficiency of inhibitors when pollutants or electrolytes are present (Chandrabhan, *et al.,* 2018).

iv. Thermodynamic Properties: MC simulations are capable of calculating thermodynamic values including the surface excess, free energy of adsorption, and adsorption isotherms. These numbers provide us a mathematical understanding of the adsorption and desorption processes, and we can use them to determine the ideal inhibitor concentrations and environmental conditions to stop corrosion to the greatest extent possible (Chandrabhan, *et al.,* 2018).

For example, in a study on the corrosion inhibition of steel by organic compounds, MC simulations can model the

adsorption and desorption of inhibitor molecules on the steel surface. By sampling various configurations and evaluating the probabilities, researchers can calculate the coverage of inhibitors, study the effect of temperature and electrolyte composition on adsorption, and determine the desorption rates. These simulations provide valuable insights into the inhibitor's behavior at the atomic level and aid in the design of effective corrosion inhibitors (Mehta, D. & Carvajal, M. A. 2019).

Quantum Mechanics/Molecular Mechanics (QM/MM) Simulations

Quantum mechanics/molecular mechanics (QM/MM) simulations are computational methods that combine the precision of quantum mechanics with the effectiveness of traditional molecular mechanics. In investigations on corrosion inhibition, both electronic and atomic-level interactions between inhibitors and metal surfaces are captured using QM/MM simulations, giving detailed insights into the mechanisms of corrosion inhibition (Liangliang, *et al.,* 2019). The system is split into two areas, the quantum mechanical region (QM) and the molecular mechanical region (MM), according to the QM/MM simulations' guiding principles. The QM region, which typically consists of the inhibitor and the metal surface, describes the active site where electrical interactions are important. The solvent and other nearby molecules are represented by the MM area, which is treated conventionally (Liangliang, *et al.,* 2019).

Studies on corrosion inhibition can use QM/MM simulations in a variety of ways.

i. QM/MM simulations make it possible to precisely calculate the electronic structures and reactivity of inhibitors. Researchers may gather comprehensive details about the electronic features, such as bond lengths, bond angles, and charge distributions, as well as compute reaction energy and barriers by characterizing the active site quantum mechanically. This knowledge is essential for comprehending how corrosion is inhibited and for creating more potent inhibitors (Rani, & Sethuraman G. 2019).

ii. Effects of the solvent on the interactions between the inhibitor and the metal surface can be accounted for by QM/MM simulations. The solvent molecules are present in the MM region, and the effects of these molecules on the active site are taken into account using conventional force fields (Moussaoui, I., & Mernari, B. 2020).

iii. Reaction Pathways: QM/MM simulations can explore reaction pathways and transition states involved in corrosion inhibition. By modeling the inhibitor-metal surface interactions, researchers can identify the key steps and intermediates in the inhibition process. This knowledge aids in understanding the mechanisms of inhibition, identifying potential reaction barriers, and guiding the development of new inhibitors with enhanced reactivity.

iv. Binding Affinities: QM/MM simulations allow for the calculation of binding affinities between inhibitors and metal surfaces. By quantifying the interaction energies, researchers can evaluate the strength of the inhibitor-metal interactions, predict binding affinities, and compare the effectiveness of different inhibitors. This information assists in the selection and optimization of corrosion inhibitors (Moussaoui, I., & Mernari, B. 2020).

For example, QM/MM simulations can shed light on the adsorption mechanisms and durability of the inhibitor on the copper surface in a study on the suppression of copper corrosion by organic molecules (Elshakre, *et al.,* 2017). Researchers can precisely model the electronic and atomic-level interactions, calculate binding energies, and forecast the inhibitory performance of various molecules by combining quantum mechanics calculations for the inhibitor and copper atoms with classical force fields for the surrounding solvent. Another example of quantum mechanics is Improving the corrosion protection properties of PVB coating by using salicylaldehyde@ZIF-8/graphene oxide two-dimensional nanocomposites (Liangliang, *et al.,* 2019).

Conclusion

The mechanics, behavior, and interactions of inhibitors with metal surfaces are elucidated in great detail using computational electrochemical approaches, which are crucial in studies on corrosion inhibition. These methods—including Quantum Mechanics/Molecular Mechanics (QM/MM) simulations, Molecular Dynamics (MD) simulations, Monte Carlo (MC) simulations, and Density Functional Theory (DFT) simulations—offer special benefits and capabilities that improve our comprehension of corrosion inhibition processes. The accurate analysis of inhibitors' electronic structures, energy levels, and reactivity is made possible by DFT calculations. They offer important knowledge on the inhibitors' stability, binding orientations, and adsorption mechanisms on metal surfaces. DFT simulations aid in the creation of more efficient corrosion inhibitors by assisting in the identification of critical parameters influencing inhibitor adsorption. The activity and interactions of inhibitors at the atomic level are better understood because to MD simulations. They make it possible to investigate the diffusion, transport, and adsorption processes, illuminating the dissemination, migration, and surface coverage of inhibitors. The investigation of inhibitor interactions with particular corrosion sites is made possible by MD simulations, which also contributes to our understanding of localized inhibition mechanisms. Statistical insights into the adsorption behavior, coverage, and competition of inhibitors are provided by MC simulations. MC simulations assist in determining surface coverage, adsorption isotherms, and inhibitor stability by simulating random adsorption and desorption processes. They offer useful details on the preferential adsorption and displacement characteristics of inhibitors when other substances are present. The precision of quantum mechanics and the effectiveness of classical molecular mechanics are combined in QM/MM simulations. They record interactions between inhibitors and metal surfaces at the atomic and electrical levels. Calculating electronic structures, reactivity, solvent effects, and binding affinities is possible with QM/MM simulations. They give in-depth explanations of reaction routes, inhibitor binding strengths, and corrosion inhibition mechanisms.

These computational methods collectively contribute to a thorough understanding of corrosion inhibition. They provide extensive atomistic information that is difficult to gain just through experimental procedures and they supplement experimental research. The development of more effective and ecologically friendly solutions to minimize corrosion in diverse industries is made possible by computational electrochemical approaches, which support the rational design and optimization of corrosion inhibitors.

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