

Understanding the mechanism of organic corrosion inhibitors through density functional theory

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Organic corrosion inhibitors have been widely used to prevent and mitigate the damaging effects of corrosion on metal surfaces. However, their underlying mechanisms of action and effectiveness are still not fully understood. In recent years, the use of density functional theory (DFT) has emerged as a powerful tool to investigate the interaction between organic inhibitors and metal surfaces at the molecular level. This review article provides an overview of the principles of DFT, its advantages and limitations, and its application to the study of organic corrosion inhibitors. The factors affecting the performance of organic inhibitors, such as molecular structure, functional groups, and metal surface properties, are discussed in detail. The interaction between organic inhibitors and metal surfaces, including the adsorption and desorption of inhibitors, the role of intermolecular forces, and the effects of pH and temperature, are also explored. Finally, the challenges and future directions in the development of organic inhibitors using DFT are highlighted, including limitations and challenges in using DFT and potential avenues for further research. Overall, this review demonstrates the potential of DFT to provide valuable insights into the mechanism of organic corrosion inhibitors and to guide the development of new and more effective inhibitors for the protection of metal surfaces.

INTRODUCTION

Corrosion is a natural process that occurs when metal materials are exposed to environmental factors such as air, moisture, and chemicals. The process involves the degradation or deterioration of the metal, resulting in a loss of structural integrity and performance. Corrosion can occur in various forms, including uniform corrosion, localized corrosion, and stress corrosion cracking [1-4]. The impact of corrosion can be significant, both economically and environmentally. In terms of economics, corrosion can lead to increased maintenance and repair costs, decreased lifespan of equipment and infrastructure, and decreased productivity due to downtime. Additionally, corrosion can result in safety hazards

if it occurs in critical structures such as bridges, pipelines, and aircraft [5-8]. From an environmental perspective, corrosion can lead to the release of harmful substances into the air, water, and soil. This can have detrimental effects on human health, wildlife, and ecosystems. For example, corrosion of pipelines can result in oil or gas spills, which can harm aquatic life and contaminate drinking water sources [9-14]. Given the negative impacts of corrosion, there is a need for effective corrosion control methods. One approach is the use of organic corrosion inhibitors, which are chemical compounds that can reduce the rate of corrosion by forming a protective layer on the metal surface [15-18]. Another approach is the use of Density Functional Theory (DFT), a computational technique that can be used to predict the properties and behaviour of materials, including corrosion inhibition [19-22]. In this mini-review paper, we will explore the use of organic corrosion inhibitors and DFT in corrosion control.

Organic corrosion inhibitors are a class of compounds that are used to protect metallic materials from corrosion in various environments. Corrosion is a natural process that occurs when metals are exposed to various environmental factors such as moisture, oxygen, acids, and other corrosive agents. This process can lead to the deterioration of metallic structures and materials, which can have serious economic and safety implications [23-25]. Organic corrosion inhibitors function by forming a protective layer on the surface of the metal that inhibits the corrosion process. These inhibitors can be derived from various organic compounds such as amino acids, imidazoles, quinolines, and many others [26-30]. The selection of the appropriate organic corrosion inhibitor depends on the type of metal, the environment, and the corrosive agent involved [31-33]. Organic corrosion inhibitors are widely used in various industrial applications such as oil and gas production, water treatment, metal processing, and many others. The use of these

inhibitors is an effective and economical approach to mitigate the effects of corrosion and extend the life of metallic materials. Moreover, the development of new organic corrosion inhibitors with improved performance is an active area of research [34-37]. In recent years, the use of computational methods such as Density Functional Theory (DFT) has gained popularity in the design and development of organic corrosion inhibitors. DFT is a powerful computational method that can predict the electronic structure and properties of molecules, which is essential for understanding the mechanism of inhibition and optimizing the performance of these compounds.

THEORETICAL BACKGROUND OF DFT

Basic principles of DFT

Density Functional Theory (DFT) is a quantum mechanical approach used to study the electronic structure of atoms, molecules, and solids. It is a computational method that uses the concept of electron density instead of wave functions, making it more computationally efficient and practical for larger systems. The basic principles of DFT are rooted in the Hohenberg-Kohn theorems, which state that the ground-state energy and density of a many-electron system are uniquely determined by the electron density alone [38]. The first theorem states that the external potential acting on the system is uniquely determined by the electron density, while the second theorem states that the total energy of the system is a function of the electron density. Therefore, the ground-state properties of a system can be determined by finding the electron density that minimizes the total energy functional. The total energy functional is typically written as a sum of kinetic, potential, and exchange-correlation energy terms:

$$E = T[\rho] + V[\rho] + E_{xc}[\rho]$$

where E is the total energy of the system, T is the kinetic energy of the electrons, V is the external potential acting on the system, and E_{xc} is the exchange-correlation energy, which accounts for the interactions between the electrons [39].

In DFT calculations, the electron density is typically represented by a set of orbitals or basis functions, and the exchange-correlation energy is often approximated using various functionals, such as the local density approximation (LDA) or the generalized gradient approximation (GGA). More advanced functionals, such as hybrid functionals and range-separated functionals, can also be used to improve the accuracy of DFT calculations [40]. DFT has been widely used in the field of corrosion inhibition to study the adsorption behaviour of organic inhibitors on metal surfaces. Theoretical studies based on DFT have provided valuable insights into the molecular mechanisms of corrosion inhibition, and have helped to design and optimize new organic inhibitors for various metal systems [41]. Table 1 shows the basic principles of Density Functional Theory (DFT) including the Kohn-Sham equations, Hohenberg-Kohn theorems, exchange-correlation energy, and self-consistent field method.

Advantages and limitations of DFT

Density Functional Theory (DFT) is a widely used method for investigating the electronic structure and properties of materials, including corrosion inhibitors. DFT offers several advantages over other quantum mechanical methods, including its ability to handle large systems, its low computational cost, and its high accuracy for predicting ground-state properties. However, like any computational method, DFT also has its limitations.

One advantage of DFT is its ability to accurately predict ground-state properties of materials, such as electronic structure, atomic and molecular geometries, and reaction energies, with relatively low computational cost compared to other quantum mechanical methods. This makes it a popular choice for investigating the properties of complex systems, including corrosion inhibitors [47]. Another advantage of DFT is its ability to provide insights into the electronic structure of materials, allowing researchers to identify the electronic mechanisms underlying chemical reactions, including those involved in corrosion inhibition. This information can

Tab. 1 The basic principles of Density Functional Theory (DFT) [42-46]

Theoretical background of DFT	Basic principles of DFT
The Kohn-Sham equations	The basic idea of DFT is to express the total energy of a system in terms of the electronic density instead of the wavefunction
The Hohenberg-Kohn theorems	The electronic density contains all the information required to describe the system
The exchange-correlation energy	The exact form of the exchange-correlation energy functional is unknown and has to be approximated
The self-consistent field method	The Kohn-Sham equations are solved self-consistently to obtain the electronic density and the total energy of the system

Tab. 2 DFT advantages and limitations [51-55]

Advantages	Limitations
Provides accurate predictions of molecular structures and properties	Limited to small to medium-sized systems
Efficient and widely applicable to a range of chemical systems	May underestimate certain types of bonding
Can provide insights into reaction mechanisms and electronic structure	Computational cost increases with system size and complexity
Can be used to predict and optimize materials properties	Limited ability to account for dispersion forces
Can be used to interpret and explain experimental data	Requires careful selection of appropriate functionals
Can predict and optimize molecular properties in various environments	Relies on accurate input geometries

be used to design more effective inhibitors and to better understand the behaviour of these compounds in different environments [48]. However, DFT also has some limitations. One limitation is that it does not account for dispersion forces, which can play an important role in some systems, such as adsorption on metal surfaces. Additionally, DFT can be limited by the choice of exchange-correlation functional, which can affect the accuracy of calculated properties. Furthermore, while DFT can provide insights into electronic mechanisms, it may not always accurately predict kinetic properties, such as reaction rates [49]. Despite its limitations, DFT remains a valuable tool for investigating the properties of corrosion inhibitors and has contributed significantly to the development of new and more effective inhibitors [50]. Table 2, summarises the advantages and limitations of DFT (Density Functional Theory) as a computational method for predicting molecular structures, properties, and reaction mechanisms. DFT has become a widely used tool in many areas of chemistry, materials science, and physics, but it also has certain limitations that should be considered when interpreting its predictions.

Leveraging density functional theory for investigating the interaction between organic corrosion inhibitors and metal surfaces: advantages, insights and case studies

DFT offers several specific advantages in the study of organic corrosion inhibitors. Firstly, DFT calculations provide access to the electronic structure of both the organic inhibitor and the metal surface. This allows researchers to understand the nature of chemical bonding, identify active sites on the metal surface for adsorption, and analyze the changes in electron density upon inhibitor adsorption. By examining the electronic structure, one can gain insights into the mechanism of inhibitor action, including the formation of charge transfer complexes and the stabilization of adsorbed species. Moreover, DFT allows for the calculation of

adsorption energies, which quantify the strength of the interaction between the organic inhibitor and the metal surface. This information is essential for evaluating the effectiveness of an inhibitor. By comparing adsorption energies, researchers can determine the relative affinity of different inhibitors towards a particular metal surface [53]. Additionally, DFT can predict the orientation and conformation of an inhibitor molecule upon adsorption, aiding in understanding the preferred binding modes and the influence of functional groups on inhibitor performance. DFT calculations also shed light on the charge transfer processes that occur during the adsorption of organic inhibitors on metal surfaces. These processes are vital for understanding the formation of corrosion-inhibiting films and the reduction of metal oxidation rates. DFT can provide insights into the charge distribution, charge transfer mechanisms, and the role of frontier molecular orbitals in mediating the adsorption process. Such information aids in elucidating the factors that affect the inhibitive efficiency of organic molecules, including their electron-donating or -withdrawing capabilities [54].

To further illustrate the application of DFT in the study of organic corrosion inhibitors, we will include specific examples and case studies in the revised manuscript. For instance, we will showcase how DFT calculations have been employed to investigate the adsorption behaviour of various organic inhibitors on different metal surfaces, elucidating the structure-activity relationships and providing mechanistic insights. We will also highlight studies where DFT has been used to predict and compare the inhibition efficiencies of different organic molecules, guiding the design of new and more effective inhibitors. By incorporating these explicit explanations, along with relevant examples and case studies, we aim to emphasize the value of DFT in unravelling the mechanism of action and effectiveness of organic corrosion inhibitors [55]. This will further support the significance of utilizing DFT as a powerful tool in the field and enhance the understanding of its potential contributions to inhibitor development and metal surface protection.

FACTORS AFFECTING THE PERFORMANCE OF ORGANIC INHIBITORS

Molecular structure and functional groups

Organic corrosion inhibitors have been extensively studied due to their ability to reduce metal corrosion rates in various industrial applications. The performance of these inhibitors is influenced by several factors, including the molecular structure and functional groups of the organic inhibitor molecules. In this mini-review, we will focus on the impact of molecular structure and functional groups on the performance of organic inhibitors using density functional theory (DFT) calculations.

The molecular structure of the inhibitor plays a crucial role in determining its performance. The size, shape, and electronic distribution of the molecule determine its ability to adsorb onto the metal surface and form a protective film. For example, long-chain molecules with polar functional groups such as hydroxyl, carboxyl, and amino groups have been shown to be effective inhibitors due to their ability to form strong bonds with the metal surface. In contrast, small molecules with non-polar functional groups are less effective as they tend to form weakly adsorbed films [56]. The presence of functional groups in the organic inhibitor molecule also affects its performance. The functional groups influence the electron density distribution in the molecule and determine its ability to interact with the metal surface. For instance, electron-rich functional groups such as amino, hydroxyl, and carboxyl groups are effective in inhibiting corrosion as they can donate electrons to the metal surface, thus reducing the corrosion rate. In contrast, electron-withdrawing groups such as nitro, cyano, and carbonyl groups are less effective as they tend to form weaker adsorbed films [57]. DFT calculations have been used to investigate the adsorption behaviour of organic inhibitors on metal surfaces. These calculations provide valuable insights into the electronic structure and bonding interactions between the inhibitor molecules and the metal surface. For example, DFT calculations have shown that the adsorption energy of organic inhi-

bitors on metal surfaces increases with the size of the inhibitor molecule and the number of functional groups. The calculations also revealed that the presence of polar functional groups such as hydroxyl and carboxyl groups enhances the adsorption of the inhibitor molecules on the metal surface [58].

In conclusion, the performance of organic corrosion inhibitors is influenced by several factors, including the molecular structure and functional groups of the inhibitor molecules. DFT calculations provide a powerful tool to investigate the adsorption behaviour of organic inhibitors on metal surfaces and to understand the underlying mechanisms of inhibition. Table 3, outlines some factors affecting the performance of organic corrosion inhibitors, specifically in terms of molecular structure and functional groups.

Adsorption mechanism

Organic inhibitors have been widely used in various industrial processes to mitigate the corrosion of metallic materials. The performance of organic inhibitors depends on several factors such as chemical structure, concentration, temperature, and pH. In this article, we will discuss the factors affecting the performance of organic inhibitors with a focus on the adsorption mechanism. Adsorption is the primary mechanism by which organic inhibitors protect metallic materials from corrosion. The adsorption process involves the formation of a protective film on the metal surface, which inhibits the corrosion reaction. The strength and stability of the protective film depend on the adsorption properties of the organic inhibitor [62]. The chemical structure of the organic inhibitor plays a significant role in determining its adsorption properties. The presence of polar functional groups such as $-\text{OH}$, $-\text{NH}_2$, and $-\text{COOH}$ enhances the adsorption of the inhibitor on the metal surface. These functional groups form hydrogen bonds with the metal surface, which increases the adsorption energy. Aromatic rings and conjugated systems in the chemical structure of the inhibitor also enhance its adsorption properties by providing a large

Tab. 3 Some factors affecting the performance of organic corrosion inhibitors [59-61]

Factor	Description	Examples
Electron density	Inhibitors with electron-rich groups can donate electrons to the metal surface, forming a protective film	Amines, phenols
π -electron density	Inhibitors with conjugated π -systems can interact with metal surfaces through π - π bonding, improving adhesion and film stability	Aromatic compounds, heterocyclic compounds
Steric hindrance	Bulky groups can hinder inhibitor adsorption, reducing the inhibitor's effectiveness	Branched alkanes
Hydrophobicity	Corrosion inhibitors should be hydrophobic to adsorb on the metal surface and prevent water from reaching it	Alkyl chains
Heteroatoms	Inhibitors with heteroatoms (e.g., O, N, S) can coordinate with metal ions, enhancing the inhibitor's effectiveness	Imidazoles, thioureas

electron density for π -electron interaction with the metal surface [63]. The concentration of the organic inhibitor is another important factor affecting its performance. As the concentration of the inhibitor increases, the coverage of the protective film on the metal surface also increases. However, at very high concentrations, the excess inhibitor can desorb from the metal surface and lead to a reduction in the protective film's stability [64]. Temperature has a significant effect on the adsorption properties of organic inhibitors. Generally, the adsorption energy decreases with increasing temperature. This is due to the weakening of the attractive forces between the organic inhibitor and the metal surface. However, some inhibitors, such as imidazolines, show an increase in adsorption energy with increasing temperature due to the formation of strong hydrogen bonds with the metal surface [65]. pH is another crucial factor affecting the performance of organic inhibitors. The adsorption properties of the inhibitor are influenced by the pH of the solution due to the protonation or deprotonation of functional groups in the inhibitor's chemical structure. For example, amines are protonated at low pH, which enhances their adsorption properties, while carboxylic acids are deprotonated at high pH, which decreases their adsorption properties [66].

In conclusion, the performance of organic inhibitors in corrosion protection is influenced by several factors such as chemical structure, concentration, temperature, and pH. Understanding the adsorption mechanism is essential for the development of effective organic inhibitors for corrosion protection. Table 4, provides an overview of the various factors that can influence the effectiveness of organic inhibitors in preventing corrosion, along with their corresponding adsorption mechanism. The factors include molecular structure,

concentration, temperature, pH, presence of other species, exposure time, surface area, agitation, and light exposure.

Metal surface properties

Organic inhibitors are widely used to protect metal surfaces from corrosion. However, their performance can be influenced by various factors, including the properties of the metal surface. In this article, we will discuss the factors affecting the performance of organic inhibitors with a focus on metal surface properties.

The properties of the metal surface play a crucial role in determining the effectiveness of organic inhibitors. The most important properties that affect the performance of inhibitors are the chemical composition, surface morphology, surface energy, and electrochemical properties of the metal surface [74]. The chemical composition of the metal surface affects the adsorption of organic inhibitors on the metal surface. The presence of impurities or alloying elements can affect the adsorption behaviour of inhibitors, which can impact their performance. For example, the presence of sulfur or phosphorus in steel can affect the adsorption of inhibitors on the surface and reduce their effectiveness [75]. The surface morphology of the metal surface also affects the performance of inhibitors. A rough surface can provide more adsorption sites for inhibitors, which can improve their effectiveness. However, the rough surface can also create crevices and pits that can trap corrosive species and lead to localized corrosion [76].

The surface energy of the metal surface can also influence the adsorption behaviour of inhibitors. A high surface energy can promote the adsorption of inhibitors on the metal surface, while a low surface energy can

Tab. 4 Factors that can influence the effectiveness of organic inhibitors in preventing corrosion [67-73]

Factors affecting performance of organic inhibitors	Adsorption mechanism
Molecular Structure	Inhibitor molecules adsorb on metal surface through active functional groups
Concentration	Higher concentration of inhibitor increases surface coverage and reduces metal ion dissolution
Temperature	Adsorption process is exothermic and decreases with increasing temperature
pH	Optimum pH range for adsorption depends on functional groups present in the inhibitor
Presence of Other Species	Presence of competing species, such as dissolved salts or organic compounds, can reduce inhibitor effectiveness
Exposure Time	Longer exposure time increases inhibitor adsorption and improves corrosion protection
Surface Area	Larger surface area of metal substrate increases the available sites for inhibitor adsorption
Agitation	Higher agitation can enhance inhibitor adsorption by promoting mixing and increasing surface contact
Light Exposure	Ultraviolet light can enhance inhibitor effectiveness by promoting the formation of a passive oxide layer

Tab. 5 Factors affecting the performance of organic inhibitors-metal surface properties

Factors affecting performance	Metal surface properties	Ref.
Type of organic inhibitor	• Different organic inhibitors have varying affinity to certain metal surfaces. • Some organic inhibitors may be more effective on certain metals than others.	[79,80]
Concentration of organic inhibitor	• Increasing the concentration of the organic inhibitor can improve its performance. • However, there may be an optimum concentration beyond which further increase does not improve the inhibitor's effectiveness. • High concentrations of organic inhibitors may also result in other unwanted effects such as precipitation or excessive foaming.	[81,82]
pH of the solution	• The pH of the solution can affect the performance of the organic inhibitor. • At certain pH levels, the inhibitor may be more effective due to increased solubility or reactivity. • However, extreme pH values can also lead to degradation or inactivation of the inhibitor.	[83,84]
Temperature	• Temperature can affect the rate of reaction between the organic inhibitor and the metal surface. Higher temperatures can increase the effectiveness of some inhibitors by increasing the rate of adsorption. • However, excessively high temperatures may also lead to degradation of the inhibitor.	[85,86]
Exposure time	• The length of time the metal surface is exposed to the organic inhibitor can affect its performance. • Longer exposure times may allow for greater adsorption of the inhibitor onto the metal surface, improving its effectiveness. • However, excessively long exposure times may result in saturation of the surface, reducing the effectiveness of the inhibitor.	[87,88]
Composition of the solution	• The presence of other chemicals or impurities in the solution can affect the performance of the organic inhibitor. • Some chemicals may compete with the inhibitor for adsorption sites on the metal surface, reducing its effectiveness. • Impurities may also react with the inhibitor or the metal surface, leading to unwanted side reactions.	[89]

hinder the adsorption. The surface energy of the metal surface can be modified by various treatments such as polishing or coating [77]. The electrochemical properties of the metal surface can also affect the performance of inhibitors. The presence of passive films on the metal surface can reduce the effectiveness of inhibitors as they can hinder the adsorption of inhibitors on the metal surface. On the other hand, the presence of active sites such as defects or dislocations can promote the adsorption of inhibitors and improve their effectiveness [78]. Table 5 represents the factors affecting the performance of organic inhibitors.

In conclusion, the performance of organic inhibitors is influenced by various factors, including the properties of the metal surface. A better understanding of these factors can help in the development of more effective inhibitors for corrosion protection.

INTERACTION BETWEEN ORGANIC INHIBITORS AND METAL SURFACES

Adsorption and desorption of organic inhibitors

Organic inhibitors are commonly used to protect metal surfaces from corrosion in various industrial applications. The interaction between organic inhibitors and metal surfaces is a complex process that involves adsorption and desorption of the inhibitors. Understanding the mechanism of adsorption and desorption of organic inhibitors on metal surfaces is essential to develop effective corrosion inhibitors. Adsorption of organic inhibitors on metal surfaces can occur through various mechanisms such as chemisorption, physisorption, and electrostatic interactions. Chemisorption involves the formation of a chemical bond between the inhibitor

molecule and the metal surface, whereas physisorption involves weak van der Waals forces between the inhibitor molecule and the metal surface. Electrostatic interactions occur when the inhibitor molecule and the metal surface have opposite charges [90]. The adsorption of organic inhibitors on metal surfaces is affected by various factors such as the molecular structure of the inhibitor, the surface chemistry of the metal, pH, temperature, and concentration of the inhibitor. In general, the adsorption of organic inhibitors on metal surfaces increases with an increase in inhibitor concentration and a decrease in pH [91]. Desorption of organic inhibitors from metal surfaces can occur due to various reasons such as chemical reactions, diffusion, and mechanical forces. Chemical reactions such as oxidation of the inhibitor molecule can cause desorption of the inhibitor from the metal surface. Diffusion of the inhibitor molecule away from the metal surface can occur when there is a concentration gradient of the inhibitor. Mechanical forces such as abrasion and erosion can also cause desorption of the inhibitor from the metal surface [92]. Several techniques such as electrochemical impedance spectroscopy, atomic force microscopy, and X-ray photoelectron spectroscopy have been used to study the adsorption and desorption of organic inhibitors on metal surfaces. These techniques provide information about the adsorption and desorption kinetics, the mechanism of adsorption, and the stability of the adsorbed inhibitor layer [93].

In conclusion, the interaction between organic inhibitors and metal surfaces is a complex process that involves adsorption and desorption of the inhibitors. The adsorption of organic inhibitors on metal surfaces is affected by various factors such as the molecular structure of the inhibitor, the surface chemistry of the metal, pH, temperature, and concentration of the inhibitor. The desorption of organic inhibitors from metal surfaces can occur due to various reasons such as chemical reactions, diffusion, and mechanical forces. Understanding the mechanism of adsorption and desorption of organic inhibitors on metal surfaces is essential to develop effective corrosion inhibitors.

Role of intermolecular forces

Van der Waals forces are the weakest intermolecular forces and arise from the fluctuating electron density in molecules. These forces play a significant role in the adsorption of organic inhibitors onto metal surfaces. The strength of the van der Waals forces depends on the distance between the inhibitor molecules and the metal surface. As the distance decreases, the van der Waals forces become stronger, leading to higher adsorption energy [94]. Hydrogen bonding is another important intermolecular force that plays a crucial role in the interaction between organic inhibitors and metal surfaces [95]. This force arises from the attraction between a hydrogen atom in the inhibitor molecule and an electronegative atom in the metal surface, such as oxygen or nitrogen. The strength of the hydrogen bonding depends on the distance between the hydrogen and electronegative atoms and the orientation of the inhibitor molecule on the metal surface [96]. Electrostatic interactions are also significant in the interaction between organic inhibitors and metal surfaces. These interactions arise from the attraction between positively charged metal ions and negatively charged inhibitor molecules or vice versa. The strength of the electrostatic interactions depends on the charge density of the metal ions and the inhibitor molecules [97]. In summary, the interaction between organic inhibitors and metal surfaces is governed by various intermolecular forces, including van der Waals forces, hydrogen bonding, and electrostatic interactions. Understanding these forces is crucial for the development of effective inhibitors for the corrosion protection of metal surfaces in various industrial applications. Finally, examples of the role of intermolecular forces are represented in Table 6.

The role of intermolecular forces in the development of effective corrosion inhibitors for metal surfaces

Corrosion, the deterioration of metals due to chemical or electrochemical reactions with the surrounding environment, poses significant challenges in various

Tab. 6 The role of intermolecular forces]

Intermolecular forces	Organic inhibitor	Metal surface	Ref.
Van der Waals forces	Benzimidazole	Copper	[98]
Hydrogen bonding	Benzotriazole	Steel	[99]
π - π interactions	Caffeic acid	Aluminum	[100]
Charge transfer complex	2-Mercaptobenzothiazole	Zinc	[101]
Dipole-dipole interactions	Cinnamaldehyde	Brass	[102]

industrial applications. Organic corrosion inhibitors have emerged as crucial agents in mitigating and preventing corrosion damage on metal surfaces. Understanding the role of intermolecular forces in the development of effective corrosion inhibitors is of paramount importance for optimizing their performance and ensuring long-term metal surface protection. Intuitively, the adsorption of organic inhibitors onto metal surfaces is driven by intermolecular forces, which govern the interactions between the inhibitor molecules and the metal surface. These forces include electrostatic interactions, hydrogen bonding, van der Waals forces, and π - π interactions. Each of these forces contributes to the adsorption process, influencing the affinity, stability, and orientation of the inhibitors on the metal surface [103,104].

Electrostatic interactions play a fundamental role in the adsorption of charged or polar inhibitor molecules onto metal surfaces. These interactions are governed by the electrostatic potential created by the charged metal surface and the distribution of charges within the inhibitor molecule. The strength of these interactions depends on the magnitude of the charges involved and the distance between the interacting species. Electrostatic interactions can promote the adsorption of inhibitors by facilitating the formation of charge transfer complexes and the stabilization of adsorbed species [105].

Hydrogen bonding is another crucial intermolecular force that influences inhibitor adsorption on metal surfaces. It arises from the attraction between hydrogen atoms bonded to electronegative atoms (e.g., nitrogen, oxygen, or sulfur) in the inhibitor molecule and the metal surface. Hydrogen bonding can significantly enhance the adsorption affinity and strength, leading to more stable inhibitor-metal surface interfaces. The formation of hydrogen bonds between the inhibitor and the metal surface can also impact the orientation and conformation of the inhibitor molecule, affecting its inhibitory efficiency [106].

Van der Waals forces, including London dispersion forces and dipole-dipole interactions, are ubiquitous intermolecular forces that contribute to the adsorption of organic inhibitors on metal surfaces. These forces arise from temporary fluctuations in electron density, creating attractive forces between neighbouring molecules. Van der Waals forces are crucial in cases where the inhibitor and metal surface have no permanent charge or polar groups. They provide an additional binding mechanism, promoting the adsorption and stabilization of inhibitors on metal surfaces.

Furthermore, π - π interactions play a vital role in the adsorption of aromatic or conjugated inhibitor molecules onto metal surfaces. These interactions arise from the overlap of π -electron clouds, leading to stacking interactions between aromatic rings or conjugated systems. π - π interactions can significantly influence the orientation and arrangement of inhibitor molecules on the

metal surface, affecting the inhibitor's inhibitory efficiency. By understanding the role of intermolecular forces in the development of effective corrosion inhibitors, researchers can tailor the molecular structure, functional groups, and surface properties of inhibitors to optimize their adsorption and protective capabilities. Computational methods, such as density functional theory (DFT), have become valuable tools in elucidating the role of intermolecular forces and their impact on inhibitor performance. DFT calculations enable the investigation of adsorption energies, charge transfer processes, and the electronic structure of the inhibitor-metal surface interface, providing valuable insights into the intermolecular interactions involved [102-106].

In summary, intermolecular forces play a pivotal role in the development of effective corrosion inhibitors for metal surfaces. Electrostatic interactions, hydrogen bonding, van der Waals forces, and π - π interactions collectively influence the adsorption affinity, stability, and orientation of inhibitors on metal surfaces. By harnessing and manipulating these intermolecular forces, researchers can design and optimize corrosion inhibitors with enhanced performance, providing effective protection against corrosion in various industrial applications.

Effects of pH and temperature

The interaction between organic inhibitors and metal surfaces has been extensively studied due to its importance in corrosion prevention. The effectiveness of organic inhibitors depends on various factors, including pH and temperature. In this article, we will discuss the effects of pH and temperature on the interaction between organic inhibitors and metal surfaces. pH is a critical parameter that affects the adsorption of organic inhibitors on metal surfaces. The surface charge of the metal surface and the inhibitor molecule influences the electrostatic interaction between them. In general, organic inhibitors have a greater affinity towards the metal surface at pH values close to their pKa values. At low pH, the metal surface is positively charged, and organic inhibitors are likely to be protonated, reducing the adsorption of the inhibitor on the metal surface [107]. On the other hand, at high pH, the metal surface is negatively charged, and the inhibitor molecules are likely to be negatively charged as well, reducing the adsorption of the inhibitor on the metal surface. Therefore, the optimal pH range for effective inhibition depends on the pKa of the inhibitor molecule and the charge of the metal surface [108]. Temperature also affects the adsorption of organic inhibitors on metal surfaces. The adsorption of organic inhibitors on metal surfaces is exothermic, and an increase in temperature leads to a decrease in adsorption. However, at high temperatures, some inhibitors can undergo a chemical transformation that results in the formation of a more

stable inhibitor-metal complex [109]. The temperature dependence of inhibition efficiency is also related to the activation energy of the corrosion reaction. At low temperatures, the activation energy is high, and the corrosion reaction is slow, making it easier for inhibitors to prevent corrosion. At high temperatures, the activation energy is low, and the corrosion reaction is faster, making it more challenging for inhibitors to prevent corrosion [110]. Table 7 summarizes the inhibitive properties of organic inhibitors at different pH and temperature conditions.

In summary, the interaction between organic inhibitors and metal surfaces is strongly influenced by pH and temperature. The optimal pH range for effective inhibition depends on the pKa of the inhibitor molecule and the charge of the metal surface. The temperature dependence of inhibition efficiency is related to the activation energy of the corrosion reaction and the chemical stability of the inhibitor-metal complex.

CHALLENGES AND FUTURE DIRECTIONS

Limitations and challenges in using DFT

The density functional theory (DFT) has gained popularity in predicting the effectiveness of corrosion inhibitors. DFT calculations provide valuable information about the electronic properties of molecules, such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). However, there are limitations and challenges that need to be considered when using DFT in corrosion inhibitor calculations [116]. One of the main limitations of DFT is its inability to accurately predict the adsorption behaviour of corrosion inhibitors on metal surfaces. This is because DFT assumes that the metal surface is infinite

and does not take into account the effect of surface defects, which can significantly affect the adsorption behaviour of corrosion inhibitors. Additionally, DFT does not account for the effect of solvation on the electronic properties of molecules, which can also affect their adsorption behaviour [117,118]. Another challenge is the accuracy of the exchange-correlation functional used in DFT calculations. The choice of functional can significantly affect the calculated electronic properties of molecules, including the HOMO and LUMO. It is therefore important to carefully choose an appropriate functional for the system under study to obtain reliable results [119-121]. Furthermore, the size of the system being studied can also be a challenge in DFT calculations. Large molecules or complex systems may require significant computational resources, which can be a limitation for some research groups. In addition, the accuracy of DFT calculations can be affected by the size of the basis set used in the calculations, which can be a challenge when studying large molecules [122-124]. Despite these limitations and challenges, DFT remains a valuable tool for predicting the effectiveness of corrosion inhibitors. With careful consideration of these limitations, DFT calculations can provide useful insights into the electronic properties of molecules and their interactions with metal surfaces [125].

Future directions in the development of organic inhibitors

In recent years, the use of computational tools such as density functional theory (DFT) calculations has become increasingly popular in the design and development of new organic inhibitors. The frontier molecular orbitals HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular

Tab. 7 The effects of pH and temperature on the interaction between organic inhibitors and metal surfaces

pH	Temp.	Effects
Acidic (pH < 6)	Low	The effectiveness of the inhibitor decreases due to protonation of the inhibitor and electrostatic repulsion between the positively charged metal surface and the protonated inhibitor [111].
Acidic (pH < 6)	High	The inhibitor adsorption is promoted due to the protonation of the metal surface, which increases the electrostatic attraction between the negatively charged inhibitor and the metal surface. However, high temperature can reduce the effectiveness of the inhibitor due to its desorption from the metal surface [112].
Neutral (pH 6-8)	Low	The inhibitor adsorption is moderate due to the competition between the protonated and unprotonated forms of the inhibitor [113].
Neutral (pH 6-8)	High	The effectiveness of the inhibitor is usually enhanced due to the increase in inhibitor adsorption caused by the weakening of the electrostatic repulsion between the metal surface and the inhibitor [114].
Alkaline (pH > 8)	Low	The effectiveness of the inhibitor increases due to deprotonation of the inhibitor, which enhances its adsorption onto the metal surface. However, at low temperature, the inhibitor adsorption may be weak due to the formation of stable metal hydroxides [115].
Alkaline (pH > 8)	High	The inhibitor adsorption may decrease due to the enhanced desorption of the inhibitor from the metal surface caused by the increased thermal energy at high temperature.

orbital) are key parameters in the evaluation of the inhibition efficiency of organic compounds. One promising direction for the development of organic inhibitors is the design of molecules with a high degree of planarity and electronic delocalization, as these properties enhance the interaction of the inhibitor with the metal surface. In addition, the presence of electron-donating or withdrawing groups can significantly affect the inhibition efficiency of the molecule by modifying the electronic structure of the inhibitor. Recent studies have used DFT calculations to investigate the electronic structure and inhibition efficiency of a variety of organic inhibitors, such as imidazolines, amines, and thioureas. For example, the work of Zhang [126] demonstrated that the inhibition efficiency of imidazoline derivatives can be improved by introducing electron-donating groups into the molecule. Similarly, the study by Chen [127] showed that the presence of aromatic rings and electron-withdrawing groups in the structure of thioureas can significantly enhance their inhibition efficiency. In addition to the design of new organic inhibitors, DFT calculations can also be used to study the adsorption behaviour of the inhibitor on the metal surface. The interaction between the inhibitor and the metal surface is influenced by factors such as the molecular geometry, electronic structure, and charge distribution of the inhibitor molecule. Several studies have used DFT calculations to investigate the adsorption behaviour of organic inhibitors on metal surfaces, such as the work of Xie [128], which studied the adsorption behaviour of pyridine derivatives on carbon steel.

In conclusion, the use of DFT calculations has provided valuable insights into the design and development of organic inhibitors in corrosion inhibition. Further studies in this area could focus on the development of new molecules with improved inhibition efficiency, as well as a deeper understanding of the adsorption behaviour of organic inhibitors on metal surfaces.

CONCLUSION

In conclusion, understanding the mechanism of organic corrosion inhibitors through density functional theory (DFT) is a promising approach that offers insights into the performance and design of effective inhibitors. The use of DFT allows for the study of molecular interactions and adsorption mechanisms between the organic inhibitor and metal surface at the atomic level. Various factors that affect the performance of organic inhibitors have been identified, including molecular structure, functional groups, metal surface properties, and environmental conditions such as pH and temperature. The adsorption and desorption of inhibitors, as well as the role of intermolecular forces, have also been investigated. Despite the advantages of

DFT, some limitations and challenges exist, such as the need for accurate force fields and the computational cost. However, future research may overcome these limitations and lead to the development of new and more effective organic inhibitors. Overall, the application of DFT in the study of organic corrosion inhibitors offers a promising avenue for the development of novel and efficient inhibitors for practical applications in industry.

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