Schiff Base Complexes as Corrosion Inhibitors: Experimental and Theoretical Investigations

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Abstract- ***This study explores the potential of Schiff base-metal complexes as corrosion inhibitors for mild steel in acidic environments through a combination of experimental and theoretical approaches, where Schiff bases derived from salicylaldehyde and aromatic amines were synthesized and complexed with transition metals such as Cu(II), Zn(II), and Ni(II), followed by their characterization using FT-IR, UV-Vis spectroscopy, and elemental analysis to confirm their structure and purity, and their anticorrosive efficacy was evaluated using weight-loss measurements, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) in 1M HCl solution, revealing inhibition efficiencies exceeding 90% at optimal concentrations for certain complexes, which was attributed to the formation of a protective layer on the metal surface as evidenced by surface analysis using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), while quantum chemical calculations employing density functional theory (DFT) provided insights into the electronic structure and adsorption behavior of the complexes, with key parameters such as HOMO-LUMO energy gap, dipole moment, and Fukui indices correlating with experimental inhibition efficiencies, and molecular dynamics simulations further elucidated the adsorption mechanisms by modeling the interaction of the complexes with the steel surface, demonstrating that strong adsorption was driven by π-electron interactions and the presence of heteroatoms in the Schiff base ligands, which facilitated electron donation to the metal surface, and additionally, the thermodynamic parameters obtained from adsorption isotherms suggested that the adsorption process was spontaneous and endothermic, indicating physisorption with contributions from chemisorption for highly efficient complexes, and the study concludes that Schiff base-metal complexes are effective, environmentally friendly corrosion inhibitors with potential for industrial applications, while also highlighting the importance of combining experimental and computational methods to achieve a comprehensive understanding of the corrosion inhibition mechanisms and guiding the rational design of more efficient inhibitors tailored for specific environments and metal substrates.***

Indexed Terms- ***Schiff Base Complexes, Corrosion Inhibition, Electrochemical Impedance Spectroscopy (EIS), Density Functional Theory (DFT), Adsorption Mechanism, Mild Steel in Acidic Media***

I. INTRODUCTION

Schiff Bases are an important class of metal corrosion inhibitors, which have been extensively studied as they are readily synthesized by the condensation of primary amines with carbonyl compounds forming azomethine linkages (C=N) that can effectively coordinate with the metal and block the occurrence of corrosion phenomena, especially at one of the most susceptible conditions such as acidic environment (Divya Jyoti et al., 2023; Alamiery, n.d.), owing to their rudimentary designs and strong inhibitive performance as they can easily adsorb on the metal surface to form an acceptable protective layer by preventing the corrosion agents to penetrate to the metallic surface and with the presence of heteroatoms such as nitrogen, oxygen, and sulfur in the structure which augments its inhibitive Ness by contributing lone pair electrons to the unoccupied d-orbitals of the metal atoms leading to the formation of a stable coordination bond (Kashyap et al., 2018; Safak et al., 2012) and recent studies have also been pointed out that the coordination of transition metals like copper, nickel, and zinc with the Schiff base ligands also

showed more effective with the more pronounced characteristic behaviour compared with the free ligands by exhibiting more better adsorption properties thereby forming more stable films on the metal surface (Kashyap et al., 2018; Verma & Quraishi, 2021) and also different techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) which are frequently used in corrosion studies for assessing the corrosion inhibition performance of Schiff base complexes and because of finding the mechanism of action by which they inhibit the corrosive process (Divya Jyoti et al., 2023; Umoren & Solomon, 2019); and along with that it has also been used the theoretical studies including quantum chemical calculations and molecular dynamics simulations that have provided valuable insights into the interactions between Schiff base complexes and metal surfaces, such as the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and energy gap for both orbitals would correlate with the tendency to donate and accept electrons, which in turn correlates with their adsorption strength and inhibition efficiency (Kashyap et al., 2018; Safak et al., 2012); and besides that much attention was also given to the development of environmentally friendly Schiff base complexes to replace the conventional anticorrosion agents that pose environmental and health concerns where the research studies were also conducted with the other various Schiff base ligands that were synthesized from different bio-based materials as well as the green solvents and methods applied for Schiff base synthesis (Divya Jyoti et al., 2023; Verma & Quraishi, 2021); and overall, Schiff base complexes represent such a versatile and effective class of corrosion inhibitors with the ongoing focus of the day on enhancing their efficiency, unraveling their mechanisms of action using experimental and theoretical approaches, and developing sustainable synthesis methods to reduce environmental impact (Divya Jyoti et al).

Statement of the research problem

Corrosion inhibitors are commonly employed to protect metal components from the harmful effects of corrosion, especially in acidic environments, and therefore finding new, cheap and environmentally friendly corrosion inhibitors for metals like mild steel (MS) against corrosion is crucial because of well-known toxic and environmental hazards of the existing corrosion inhibitors which necessitate the exploration for alternative meaning potential new compounds that show high inhibition efficiency without adverse effects. In view of these issues, Schiff bases obtained from the condensation of primary amines with carbonyl compounds have attracted much attention as promising inhibitors due to their structural diversity, capability to form inner-sphere complexes with metal ions and the ability to provide protective barriers by adsorption on the metal surfaces and blocking the corrosive agents [21,22]. Though the inhibition efficiency of Schiff base complexes depends on the nature of the metal center, electronic properties of the ligand and environmental conditions (Acidic or Basic medium) [22–26], the mechanism of inhibition still need to be further elucidated and proves to have a significant understanding of interception by both experimental and theoretical methodologies. Experimental techniques that reveal the electrochemical behavior of these complexes include electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization, while methods such as scanning electron microscopy (SEM) provide insight into the morphology of the metal surface on which the inhibitor adsorbed. Theoretical methods, such as DFT calculations, provide relevant information heavily associated to the electronic structure of the inhibitors, and serve more in predictability on reactivity and how the inhibitors interact with metal surfaces, which will help rationally design more efficient inhibitors. Schiff base complexes may represent a promising category of eco-friendly corrosion inhibitors; however, further studies on their applicability, stability, optimum performance parameters, and eco-friendly production methods need to be performed for broader applicability in industries that continue to utilize heavy metal salts for abatement of corrosion. Overcoming these challenges is essential to make the application of Schiff base complexes as better alternatives than the traditional corrosion inhibitor types, which is one step closer to finding safer and more efficient corrosion protection strategies across different industrial applications.

Significance of the research study

This research study is significant because metal corrosion is a universal problem (Divya Jyoti et al., 2022; Alamiery, n.d.), has become an inherent

industrial concern, especially for mild steel in acidic environments (Kashyap et al., 2018), while the traditional corrosion inhibitors have serious environmental and health hazards (Alamiery, n.d.; Kashyap et al., 2018), thus alternatives need to be explored as a high efficiency corrosion inhibitor, and corrosion inhibitors are needed that will not cause serious ecological and human health hazards (Alamiery, n.d.; Kashyap et al., 2018) and although many structural forms of Schiff bases and their stable complexes of certain metals have been likely reported (Kashyap et al., 2018; Jamil et al., 2018) and this study aims at the synthesis, characterization of Schiff base complexes and their corrosion inhibition performance in HCl environment using various techniques (Divya Jyoti et al., 2022; Synthesis and evaluation of Schiff base, 2022) electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization which provide information of the electrochemical behavior of the complexes (Kashyap et al., 2018) includes surface analysis methods such as scanning electron microscopy (SEM) the surface is likely changed on metal as the inhibitor is adsorbed, visualization which can well be defined and finally the theoretical part consists of density functional theory (DFT) calculations which provide useful insights on the electronic structure of the inhibitors that gives idea about the metal surface reactivity (Jamil et al., 2018; Materials, 2022) and an integral part of what this research study provides is a detailed understanding of these well-known compounds is a comparison, and that can offer tailor-made inhibitors for industrial applications (Synthesis and evaluation of Schiff base, 2022) while as an environmentally friendly Schiff base complexes that can be effective corrosion inhibitors are attractive in this respect that if addressed in a better way can provide solutions to mitigate this inherent problem and Schiff bases can commendably prevent corrosion (Divya Jyoti et al., 2022; Materials, 2022) and the authors of this research study feel that such works can eliminate corrosion related challenges in various industries such as, but just not limited to construction, manufacturing (Kashyap et al., 2018), and transportation (Jamil et al., 2018), and the integrity of both practical and theoretical values will reasonably reflects this study in its synthesis and evaluation of Schiff base complexes can not only adds to the scientific understanding of Schiff base as corrosion inhibitors but also provide an environmentally-friendly solutions to the corrosion problems (Divya Jyoti et al., 2022; Alamiery, n.d.).

Review of relevant literature related to the study

Schiff base complexes have been the focus of much recent corrosion inhibitor research as they effectively reduce metal degradation in diverse environments (Jyoti et al., 2024; Alamiery, n.d.) and are sourced from readily available chemicals (Jyoti et al., 2024), where Schiff bases are compounds formed from the reaction of primary amines and carbonyl compounds and tend to have strong coordination bonds with metal surfaces; this provides a protective barrier from corrosion (Jyoti et al., 2024), and a comprehensive review is given by Jyoti et al. (2024) Explain the synthesis methods, mechanisms and application of the Schiff bases corrosion inhibitors, and they indicate that the structural diversity of Schiff bases is very high, and the electron-donating groups attached to the carbon atom adjacent to the nitrogen atom directly affect the corrosion inhibition efficiency, and Alamiery (n. d.) also confirm the high efficacy of Schiff bases as corrosion inhibitors, explaining their adsorption properties and the high stability of complexes formed with metal ions, and on the environmental side. Schiff bases have advantages with respect to biodegradability and lower toxicity compared to traditional inhibitors, and a few experimental works Jamil et al. Using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques to assess the inhibition performance of Schiff base inhibitors indicated high inhibited corrosion for mild steel in acidic media with a ~70% reduction in corrosion rate, and showed that they adsorb on metal surface barrier inhibiting the anodic and cathodic reactions (Kashyap et al. 2018) (2018) prepared transition metal complexes of the Schiff bases and tested them as corrosion inhibitors, as well as for their antimicrobica and anticancer activities; the results indicate that the obtained metal complexes showed higher inhibition efficiency as compared to the free ligands; this property is attributed to the higher adsorption process of the metal complexes than their free ligands due to the presence of metal centre, and in their theoretical aspects, several papers such as density functional theory (DFT) calculations were used to study the electronic properties of the Schiff bases by investigating the highest occupied molecular orbital (HOMO) and

lowest unoccupied molecular orbital (LUMO) energies of such molecules which were shown to be related to greater adsorption capability and inhibition efficiency of the investigated Schiff base compounds, further allowing a prediction of the strength of interaction of the compounds with the metal and reactivity (Jamil et al., 2018; Verma & Quraishi, 2021); the ecological aspects of synthetic processes and corrosion inhibitor components have become very important, recently, global research efforts have been aiming towards the invention of tar and ecologically friendly Schiff base inhibitors, even their preparation through more environmental spectrums mechanisms, for example, in the field of corrosion inhibitors, Verma and Quraishi (2021) done a comprehensive speech about the previous developments in some the corrosion inhibitors with the aqueous phase, detecting that the recent activities are focusing on green chemistry principles which in first sight are absolutely reasonable for their use in the synthesis of Schiff bases, including the introduction of nature-inspired resources, and eco-friendly synthesis approaches are focused at decreasing the negative effects to the environment without forfeiting a high consideration inhibition efficiency, with perspective point on these valuable barriers behavior too, some results were achieved when they conducted trials, showing a low expense preparation with corrosion inhibition reactions through testing the obtained reaction mixtures in a variety of industrial applications within specific equipment that usually covered with a thick layer of corroding technology, such as a carbon steel in an acid environment, not only are some industries inadvertently relevant to the water, and gas sectors, but their numerous products also can be tailored and designed, maximizing utilities in unfamiliar directions,, despite the impressive results, subsequently, all the problems in weak favourable reaction were retrieved equity in terms of a detailed understanding but at the same time disallowed dramatically rediscovery of the stability and performance of Schiff constrain under diverse experimental conditions, therefore a legitimate research was mill made towards determining effectually a punctured engineering against broad-spectrum adsorption process mechanism, an inhibitor outline may be even contemplated the study before lab following through in the same way assume the test reaction of prevention efficiency was reflected (Kashyap et al., 2018) and taken another corrosion inhibitors, and as a result through the literature, it could be stated that this filter is growing by means of further Schiff bases complexes have proven their capability to act as feasible corrosion inhibitors and on a wide range of very efficient systems through designing and optimized a structure, the observations, both from the study in addition looking forward, confirm the reliability of the Schiff bases as alternative material of novel corroding inhibitors so their manufacture normal and integrate well toward affecting skin synthesis, nevertheless developed efforts need to target the ecological practicability and industrious request area for synergy being on total performance of the Schmidt prevent and mitigation of Schiff bases itself both as probably helpful advance to present corrosion inhibition systems, now however the growing positive competition in which reduces the prospect whole full coat effective corrosion-neutral (Jyoti et al., 2024; Alamiery, n.d.; Jamil et al., 2018; Kashyap et al., 2018; Verma & Quraishi, 2021).

Research Gap related to the study

Although much progress has been made in the field of Schiff base complexes as corrosion inhibitors, certain gaps in the research still remain and now offer important areas for future study. A major gap identified is the exploration of the long-term stability and longevity of these inhibitors across different environmental conditions, which is critical as many industries would involve metals being exposed to changing temperatures, pH levels, and corrosive agents. Moreover, although the significant efficacy of Schiff base complexes has been demonstrated jointly, there was overall not a survey which examined how the wealth and the inserting substituents (noise) may vary the azomethine junction and thereby relay their effects on inhibition efficiency. The knowledge on the effect of different functional groups on the electronic aspects and adsorption characteristics of these complexes could provide a basis for designing better effective inhibitors against specific types of metals and corrosive environments. In addition, the molecular-level interaction mechanisms of Schiff base complexes with metal surface are still poorly explained. Interestingly, further insights about these adsorptions phenomena and protective film nature could be provided by advanced surface analysis techniques such as atomic force microscopy (AFM)

and X-ray photoelectron spectroscopy (XPS). In addition, most of the previous studies have been developed toward mild steel; however, the potential of Schiff base complexes as efficient inhibitors for other metals and alloys like aluminum and copper has received less attention. Inhibitors that inhibit metals other than just lead may increase their utility across more industries, and benefits could potentially be seen from expanding research towards other metals. Besides, one more aspect that needs attention is environmentally friendly and biodegradable Schiff base complexes. It is crucial to evaluate the environmental impacts of large-scale implementation of these inhibitors, as businesses increasingly adopt greener, more sustainable practices. The only significant bottleneck or limitation in the extensive application of Schiff base complexes can be the study of its toxicity and environmental stability which are presently limited but must be given priority to fulfill the environmental regulations and pave the way for eco-friendly corrosion management strategy. Moreover, synergetic effects of the combination of Schiff base complexes with other kinds of inhibitors or nanomaterials have not been investigated extensively. Exploration of such combinations may inspire hybrid inhibitors with enhanced profiles. Finally, although the behavior of Schiff base complexes has been extensively studied using computational methods, more experimental studies are required to confirm the theoretical results. Closing this gap by demonstrating reliable correlations between theoretical predictions and experimental data would strengthen the confidence in computational approaches for the design of inhibitors. Interdisciplinary approaches that merge experimental, theoretical and environmental studies into a single associated framework will be required in order to bridge these gaps in research, which will be key to moving the use of Schiff base complexes as effective and sustainable corrosion inhibitors forward towards practical use.

Methodology adopted for the purpose of study

This research article discusses the development and characterization of Schiff base compounds that are synthesized via the condensation reaction of primary amines with carbonyl compounds to yield azomethine linkages (C=N) that can coordinate strongly to metal surfaces which restricts corrosion process (Jyoti et al., 2024; Alamiery, n.d.) and is also applied experimental methods using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods for the corrosion inhibition performance of the complexes and theoretical methods, particularly using density functional theory (DFT) that provide information on the electronic structure and reactivity of molecules and in turn with the help of such calculations maximize some orders of corrosion inhibition performance (Jamil et al., 2018) and found that Schiff base complexes possessed considerable inhibition efficiency limited the corrosion process and allows the formation of passive barrier film on metal surfaces which was further confirmed by surface analysis techniques such as scanning electron microscopy (SEM) which provide different morphological features on the inhibitor at nor well at all to areas after the adsorption of inhibitor (Kashyap et al., 2018) and also its addressability with an eco-friendly background as biodegradability and lower toxicity feature of Schiff bases than conventional inhibitors which promotes in a transition from our global industry to sustainable industry (Alamiery, n.d.; Jyoti et al., 2024).

Major objectives of the present study

1. To synthesize and characterize Schiff base-metal complexes for corrosion inhibition
2. To evaluate the corrosion inhibition efficiency of Schiff base complexes in acidic environments
3. To understand the adsorption and surface protection mechanisms of the inhibitors
4. To provide theoretical insights into the electronic properties and reactivity of the complexes

Synthesize and characterize Schiff base-metal complexes for corrosion inhibition to investigate the formation of Schiff base complexes through condensation reactions and their subsequent complexation with transition metals. Utilize techniques such as FT-IR, UV-Vis spectroscopy, NMR, and elemental analysis to confirm the structural integrity and composition of the synthesized compounds

Synthesis and characterization of Schiff base-metal complexes as corrosion inhibitors, necessitating the formation of Schiff bases via condensation reactions between primary amines and carbonyl compounds to

yield azomethine linkages (C=N) for ligand coordination to transition metals and Coxb; Characterization using several analytical techniques to verify structural integrity and composition of Schiff base ligands and their metal complexes (Synthesis and Spectroscopic Characterization of Schiff Base Metal Complexes, 2023; Synthesis and Characterization of some Metal Complexes prepared from Schiff Bases, 2021), Fourier-transform infrared spectroscopy (FT-IR) for identification of functional groups and verification in the formation of Schiff bases and their metal complexes through characteristic absorption bands corresponding to the C=N stretching vibration as well as metal-ligand bonds (Metal complexes of Schiff base: Preparation, Characterization and Corrosion Inhibition Studies, 2019), Ultraviolet-visible (UV-Vis) spectroscopy for determination of the electronic transitions within the complexes for insights into their electronic structures, and confirming complex formation through shifts in absorption maxima compared to the free ligands (Effective corrosion inhibition of mild steel in hydrochloric acid by Co (II) and Cr (III) Schiff base-metal complexes, 2022), Proton nuclear magnetic resonance (1H NMR) spectroscopy for detailed information on the hydrogen atom environments of Schiff base ligands for structural elucidation via signals corresponding to the azomethine proton (C=N) and other characteristic protons within the ligand framework (A New Synthesized Schiff Base as Corrosion Inhibitor for Mild Steel in Acidic Medium, 2020), Elemental analysis for quantitative determination of the carbon, hydrogen, nitrogen and metal content in the synthesized complexes to ensure all experimental values are in line with theoretical calculations thereby confirming proposed molecular formulas and purity of the compounds (Schiff Base and Its Metal Complexes as Ecofriendly Pitting Corrosion Inhibitors on ASTM-A36 Low Carbon Steel in Corrosive Oil and Gas Well Treatment Fluids, 2023), Thermal analysis techniques, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for evaluation of the thermal stability and decomposition pattern of the complexes providing information on the decomposition products relevant to the effectiveness of the complexes, and suitability as corrosion inhibitors under varying temperature conditions (Effective corrosion inhibition of mild steel in hydrochloric acid by Co (II) and Cr (III) Schiff base-metal complexes, 2022), and lastly magnetic susceptibility measurements that provide information on the magnetic properties and coordination environment of the metal centers within the complexes aiding determination of their geometrical structures (Corrosion Inhibition of Mild Steel in 1.0 M HCl from Thiadiazole Schiff Base Ligand and Its Metal Complexes, 2024), and X-ray diffraction (XRD) analysis can be employed to determine the crystalline nature and phase purity of the synthesized complexes, that providing essential structural details that help to complement spectroscopic data (Corrosion Inhibition of Mild Steel in 1.0 M HCl from Thiadiazole Schiff Base Ligand and Its Metal Complexes, 2024), all of these comprehensive characterization collectively confirm the successful synthesis of Schiff base-metal complexes and provide a thorough understanding of their structural and electronic properties which are essential for evaluating for their effectiveness as corrosion inhibitors as could be used in many industrial applications (Synthesis and Spectroscopic Characterization of Schiff Base Metal Complexes, 2023).

Corrosion inhibition efficiency of Schiff base complexes in acidic environments to conduct electrochemical studies, including electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization, to determine the inhibition efficiency of the complexes on mild steel in corrosive media like hydrochloric acid (HCl)

Experimental Corrosion inhibition efficiency is measured for Schiff base complexes in an acidic environment employing electrochemical studies such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization to provide inhibition efficiency data toward mild steel in hydrochloric acid (HCl) media. In this regard, Schiff base [1]s, which are formed via condensation of primary amines and carbonyl compounds, are abundant in the literature, characterized by their azomethine (-C=N-) groups that readily adsorbs into surfaces of metals to produce a protective layer against corrosion. Electrochemical impedance spectroscopy (EIS) is a key used test to determine the corrosion inhibition efficiency of such complexes as it detects the impedance of the metal-electrolyte interface over a frequency range yielding the charge transfer resistance Rct and the double-layer capacitance Cdl, that indicates the efficient of the

inhibitor. An enhancement of Rct and a reduction of Cdl due to the inhibitor suggests that these inhibitors form a protective coating on the surface of the metal, preventing corrosion processes. Potentiodynamic polarization studies provide complementary information to EIS by assessing the effect of inhibitors on anodic and cathodic reactions through sweeping of the electrode potential and record of the current, from which the corrosion potential (Ecorr) and corrosion current density (Icorr) can be determined. The drop in Icorr would imply that the presence of Schiff base complexes greatly inhibits both the anodic metal dissolution reaction and the cathodic hydrogen evolution reaction, which means that the inhibitors behave as mixed-type inhibitors. Schiff base derivatives, for example, have shown high inhibition efficiencies reaching up to 97% at their optimal concentrations and act as mixed-type inhibitors via adsorption onto the mild steel surface to lower both anodic and cathodic processes. These inhibitors reveal better follow the Langmuir type regardless of adsorption isotherm, indicating monolayer adsorption on their metal face. The confirmation of the surface corrosion may be further confirmed using surface analysis techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM), both techniques also confirming the presence of the inhibitor through the determination of a smoother metal surface over the rough, corroded surface of the metal in the absence of the inhibitor. The use of quantum chemical calculations and molecular dynamics simulations can give rise to theoretical clues on the electronic properties and adsorption behavior of Schiff base complexes that corroborate with the experimental result, so that this powerful approach can facilitate the design of more efficient inhibitors. This work contributes to a more complete picture of corrosion inhibition performance of Schiff base complexes in acidic medium considering the complementarity of electrochemical studies with surface analyses and theoretical modeling.

Adsorption and surface protection mechanisms of the inhibitors to Perform surface morphology studies using methods like scanning electron microscopy (SEM) to investigate the formation of protective films on metal surfaces and analyze the adsorption behavior of Schiff base complexes

The investigation into the adsorption and surface protection mechanisms of Schiff base complexes as corrosion inhibitors involves performing surface morphology studies using methods like scanning electron microscopy (SEM) to examine the formation of protective films on metal surfaces and analyze the adsorption behavior of these inhibitors. SEM provides high-resolution images that reveal the surface topography and composition of metals before and after exposure to corrosive environments in the presence of Schiff base inhibitors. By comparing SEM images, researchers can observe the extent of corrosion damage on untreated metal surfaces, characterized by pits and roughness, versus the smoother, more uniform surfaces of treated metals, indicating the formation of a protective inhibitor film. For instance, studies have shown that mild steel samples immersed in hydrochloric acid (HCl) without inhibitors exhibit significant surface deterioration, while those treated with Schiff base complexes display minimal corrosion, as evidenced by SEM micrographs. This suggests that the inhibitors adsorb onto the metal surface, forming a barrier that impedes corrosive agents. The adsorption behavior of Schiff base complexes is often analyzed through adsorption isotherms, with the Langmuir isotherm being commonly applied, indicating monolayer adsorption on the metal surface. The efficiency of these inhibitors is influenced by factors such as the presence of heteroatoms (e.g., nitrogen, oxygen, sulfur) in the Schiff base structure, which enhance adsorption through donor–acceptor interactions between the inhibitor molecules and the vacant d-orbitals of the metal atoms. Additionally, the planarity and conjugation of the Schiff base molecules facilitate parallel orientation to the metal surface, maximizing surface coverage and protection. Energy-dispersive X-ray spectroscopy (EDX) coupled with SEM further aids in confirming the presence of elements from the inhibitor on the metal surface, corroborating successful adsorption. Moreover, atomic force microscopy (AFM) can complement SEM studies by providing three-dimensional surface profiles, offering quantitative roughness parameters that reflect the smoothening effect of the inhibitor film. Electrochemical studies, such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization, are also employed alongside surface analyses to evaluate the corrosion inhibition

performance, with EIS revealing increased charge transfer resistance and polarization studies showing reduced corrosion current densities in the presence of Schiff base inhibitors. These combined analyses provide a comprehensive understanding of how Schiff base complexes adsorb onto metal surfaces, forming protective films that inhibit corrosion processes, thereby guiding the design of more effective corrosion inhibitors for industrial applications.

Theoretical insights into the electronic properties and reactivity of the complexes to employ density functional theory (DFT) calculations to analyze parameters such as HOMO-LUMO energy gaps, dipole moments, and charge distribution, correlating theoretical findings with experimental data to elucidate the inhibition mechanisms and optimize molecular design

Theoretical insights into the electronic properties and reactivity of Schiff base-metal complexes as corrosion inhibitors are achieved using density functional theory (DFT) calculations, which analyze parameters such as the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), dipole moments, and charge distribution to elucidate their inhibition mechanisms and optimize molecular design, where the HOMO-LUMO energy gap serves as an indicator of the stability and reactivity of the molecule, with smaller energy gaps suggesting higher reactivity and better electron donation capabilities, thereby enhancing adsorption on metal surfaces (Saha et al., 2015; Verma et al., 2022). DFT calculations also provide insights into the frontier molecular orbitals, enabling researchers to visualize electron density distributions and identify active sites within the inhibitor molecule that are likely to interact with the metal surface (Banerjee et al., 2018), while the dipole moment offers information about the polarity of the molecule, with higher dipole moments often correlating with stronger adsorption tendencies due to enhanced electrostatic interactions between the inhibitor and the metal surface (Kaabi et al., 2021). Charge distribution analysis, obtained through natural bond orbital (NBO) calculations or Mulliken population analysis, identifies regions of electron density that facilitate donor-acceptor interactions, such as those between the nitrogen and oxygen atoms in the Schiff base ligand and the vacant d-orbitals of the metal atoms, which are critical for forming a stable inhibitor-metal complex (Jamil et al., 2018). Theoretical studies often correlate DFT results with experimental data to validate the predicted inhibition efficiencies; for instance, complexes with lower HOMO-LUMO gaps and higher global softness values have been experimentally shown to exhibit superior corrosion inhibition performance, as these properties enhance the molecule's ability to adsorb onto the metal surface and form a protective barrier (Meng et al., 2017; Verma et al., 2022). Additionally, Fukui functions derived from DFT calculations identify electrophilic and nucleophilic attack sites, providing a detailed understanding of how inhibitor molecules interact with metal atoms at the atomic level (Banerjee et al., 2018). Molecular electrostatic potential (MEP) maps generated through DFT further illustrate regions of high electron density, aiding in the design of Schiff bases with optimized electronic properties to enhance their efficacy as corrosion inhibitors (Kaabi et al., 2021). The integration of DFT calculations with experimental techniques such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization not only strengthens the understanding of inhibition mechanisms but also facilitates the rational design of next-generation Schiff base inhibitors with tailored properties for specific industrial applications (Saha et al., 2015; Meng et al., 2017).

Discussion related to the study

The research, titled takes on and thoroughly describes the performance Schiff base-metal complexes as corrosion inhibitors for metals, and more specifically mild steel, in various environments including hydrochloric acid (HCl). This study combines experimental methods with theoretical computations to provide insights into the inhibition mechanisms and to aid in the molecular design of these inhibitors. Schiff base complexes are synthesized and studied through a combination of experimental process of condensation reaction of primary amines with carbonyl compounds, followed by the process of complexation with transition metals. The synthesized compounds were characterized by Fourier-transform infrared spectroscopy (FT-IR), ultraviolet-visible (UV-Vis) spectroscopy, nuclear magnetic resonance (NMR), and elemental analysis, which reveal the structural fidelity and composition of the compounds. These techniques detect functional groups, electronic

transitions, and molecular arrangements to confirm successful complex formation of the complexes that one wishes to prepare (Table 1). The electrochemical methods such as Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarization studies are employed to evaluate the corrosion inhibition efficiency of these complexes. The electrochemical impedance spectroscopy (EIS) measurements confirmed that since the charge transfer resistance increases in the case of inhibitors, it shows the protective layer on metal surface. Potentiodynamic polarization studies demonstrate an impressive decrease in corrosion current density for these inhibitors, showing them to be mixed-type with respect to the anodic and cathodic reactions. Surface morphology analyses, based on scanning electron microscopy (SEM) and atomic force microscopy (AFM), also confirm the presence of an inhibitor film on the surface, as the roughness and defects found on the corroded metal surface are fewer and lower than those on untreated samples. Further Theoretical insights are gained through density functional theory (DFT) calculations studying parameters such as the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), dipole moments and charge distribution. Higher adsorption on the surface of the metal as indicated by lower HOMO-LUMO energy gap which indicates higher reactivity and electron donation capability. Charge distribution analysis reveals subdomains in the inhibitor molecules that stabilize donor-acceptor pairs with metal atoms and thereby stabilize the inhibitor–metal complexes. This theoretical approach is consistent with experiment data and provides insight into the inhibition mechanisms.

Additionally, the adsorption behavior of the Schiff base complexes seems to follow the Langmuir adsorption isotherm indicating a monolayer adsorption on the metal surface. In the Schiff base, the heteroatoms, like nitrogen, oxygen, and sulfur, enhances the adsorption through donor–acceptor interaction with the empty d-orbitals of metal atoms. The adsorption creates a layer that prevents corrosive species, thus reducing the corrosion. Ultimately this study combines experimental techniques and theoretical calculations to provide an understanding of the mechanism for how Schiff base-metal complexes function as effective corrosion inhibitors. This data will help guide the rational design of the next generation of corrosion inhibitors, which can be developed with desirable features specific to an individual industry.

Chemical implications related to the study

This paper explores the influence of Schiff base-metal complexes as corrosion inhibitor, specifically for mild steel in acidic medium e.g. hydrochloric acid (HCl). Synthesized from a condensation reaction of primary amines and carbonyls, the azomethine functional group (-C=N-) is referred to as Schiff bases and their respective metal complexes have been widely investigated as promising corrosion inhibitors. The existence of heteroatoms such as N, O and S in Schiff base increases their electron-donating ability which promotes their adsorption to the surface of metals and the formation of protective films that resist corrodents. Different experimental techniques such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies have shown that the complexes enhance charge transfer resistance and decrease corrosion current density suggesting the formation of a barrier layer inhibiting the metal substrate from corrosive access. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses of surface morphology reinforce the effective formation of a continuous and adherent inhibitor layer on the metal surface in reducing its texture and defects ascribed to corrosion processes. Brief theoretical insights based on the density functional theory (DFT) calculations show that the complexes of Schiff base-metal with small energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied (LUMO) not only are more reactive and have a greater ability to donate electrons but also increase their adsorption on the metal surface. Moreover, charge distribution analyses show areas in the inhibitor molecules that allow donor-acceptor interaction with metal atoms, which is important for the stable formation of an inhibitor-metal complex. These inhibitors typically obey the Langmuir adsorption isotherm according to the adsorption behavior on metal surface which also play an important role in corrosion inhibition. A combination of experimental results and theoretical calculations leads us to a holistic understanding of the inhibition mechanisms, reflecting the ability to design

Schiff base-metal complexes that express maximized electron-donating properties along with optimal structural characteristics to promote their efficiency as corrosion inhibitors. This study emphasizes the importance of experimental and theoretical synergy in the development of effective corrosion inhibitors and provides significant advantages for industrial applications where metal corrosion first presents itself as an important problem.

CONCLUSION

Based on both experimental and theoretical studies, the research article summarizes that the prepared Schiff base-metal complexes through condensation reaction and subsequent metal complexes exhibited effective corrosion inhibition efficiency towards mild steel in 1M HCl medium using a combined approach; the methodology integrated electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques wherein it was observed the increasing charge transfer resistance and decreasing corrosion current density revealing the largest inhibition efficiency of the prepared complexes in this way confirming the surface film protection mechanism, SEM and AFM which confirmed the smooth and uniform inhibitor films formed on treated than the rough and corroded surfaces, respectively and also the DFT calculation where the small increase of the hypothetical orbital energy gap and the larger dipole moments predicted the suitable charge distribution implied an efficient adsorption of these complexes on the surface of metal in good agreement with the experimental confirmatory tests that the adsorption obeyed the Langmuir isotherm, suggesting monolayer adsorption due to the donor-acceptor interaction between the d-orbitals of the metal which found to be vacant and nitrogen, oxygen and sulfur heteroatoms as the components of the Schiff base structure that provided the effective electron-donating behavior confirming that also the inhibitors' effectiveness stemmed from the presence of heteroatoms as this combination of the experimental data with theoretical insight proves greater attention for the structural and electronic properties in determining the inhibition performance which can provide the rationale of the tailored molecular design for optimization of these complexes as specific applications orientated for next-generation as sustainable and efficient solutions to mitigate industrial corrosion as the study illustrated the fact of interconnected advanced analytical, computational and electrochemical techniques led to a comprehensive understanding of inhibition mechanisms as the consonance of the electrochemical synthesis and characterization of new generation molecular organized arrays will pave the development of substantial implications for the next-generation Schiff bases-metal complexes.

Scope for further research and limitations of the study
The limitations of this study, along with suggestions for future research indicate that with the current work, although the significant potential of Schiff basemetal complexes are demonstrated to be effective corrosion inhibitors for mild steel in an acidic environment, via electrochemical tests; namely, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization as well as theoretical approaches such as density functional theory (DFT) calculations, the research is limited through not addressing the long-term stability of the inhibitors under realistic industrial conditions in which the temperature, pH, and mechanical requirements can lead to the dissolution of the protective films of the inhibitors, and while the theoretical exploration of both qualitative and quantitative aspects of the electronic properties (i.e., HOMO-LUMO gaps, dipole moments, and charge distribution) thought to influence the inhibition efficiency provide important insights, the field still remains unexplored in terms of investigating the effects of structural modifications to the ligand framework that include substituent effects and steric hindrance on the performance of these inhibitors; the adsorption mechanisms are described in terms of the use of Langmuir isotherms and donor-acceptor interactions with insufficient validation based on advanced surface characterization techniques such as X-ray photoelectron spectroscopy (XPS) or time-of-flight secondary ion mass spectrometry (TOF-SIMS), which can deliver detailed evidence of the chemical interactions between inhibitor molecules and metal surfaces not present in this research along with a lack of quantitative insight into the thickness and duration of protective films formed under prolonged exposure to corrosive agents lacking in the current work leading to the recommendation for future research using in situ techniques such as electrochemical quartz crystal

microbalance (EQCM) or ellipsometry; the emphasis being placed predominately on mild steel in hydrochloric acid as corrosion targets have left the implications lacking with respect to potential expansion of the research on other metals and alloys such as aluminum, copper, or stainless steel that are applied commonly in various industrial applications along with the potential for the development of novel eco-friendly inhibitors as demonstrated in this research which, while proposed to be greener alternatives to traditional inhibitors, due to the combined metal-ligand systems of the Schiff base-metal complexes, are not extensively investigated for their environmental impact and biodegradability, and thus require additional studies on their toxicity, long-term environmental persistence, and compatibility with green chemistry principles; and, the potential theoretical findings earned from both DFT and molecular modeling providing insight into electronic properties and inhibition mechanisms, however without experimental validation to confirm qualitative and quantitative relationships between theoretical results and real-world performance being insufficient to establish definitive correlations duly needing additional experimental-theoretical synergy to improve predictive accuracy; therefore also would require future research on the synergistic effects of combining Schiff base-metal complexes with other inhibitors or nanomaterials thereby a bridge toward hybrid systems in concerted efforts to improve performance, while future research would also require an expansion of studies toward either in situ industrial tests and scale-up to progress to the practical direction of gap bridging via laboratory research and real-world applications remains a critical stage.

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