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About Structure and Activity of Zwitterionic Schiff Base Inhibitors for Steel Corrosion in Acidic Media

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***Abstract*—Zwitterionic Schiff base derivatives have emerged as excellent corrosion inhibitors thanks to their particular ability to adsorb aggressively on metal surfaces. This chapter analyzes the inhibitory performance of two iminium-enolate zwitterions and one hydroxyl-containing zwitterionic analogue on carbon steel in 1M H_2SO_4. Potentiodynamic polarization and adsorption investigations reveal that all chemicals function as mixed-type inhibitors and adhere to the Langmuir adsorption isotherm. The inhibitory efficiencies and thermodynamic characteristics are linked to molecule structure and substituent effects. The hydroxyl-containing derivative has the strongest adsorption and inhibitory efficiency, indicating a clear structure-activity link.**

***Keywords*— Zwitterionic Schiff bases; Iminium–enolate; Corrosion inhibition; Carbon steel; Sulfuric acid; Langmuir adsorption; Tafel polarization**

I. INTRODUCTION

Because of its advantageous mechanical qualities and cost-effectiveness, carbon steel is widely utilized in industrial applications. Nevertheless, it is extremely prone to corrosion in acidic conditions like sulfuric acid, which is frequently used in pickling, descaling, and acid cleaning processes [1]. Effective corrosion mitigation techniques are required because acidic media's aggressiveness speeds up the breakdown of metals. Adsorption at the metal–solution interface largely controls the efficacy of organic corrosion inhibitors, which are still among the most practicable options. Molecular structure, electrical distribution, and the existence of heteroatoms and conjugated systems that can interact with the steel surface are all important factors in this adsorption.[2][3].

Because of their great adsorption ability and structural tunability, schiff bases, which are defined by the azomethine (–C=N–) activity, have been extensively studied [4][5]. Since the coexistence of cationic and anionic centers within the same molecule promotes stronger and more stable adsorption through combined electrostatic interactions, coordination bonding, and π-electron donation, especially in acidic media, zwitterionic Schiff base derivatives have garnered more attention in recent years.
[2–6].

In order to shed light on the structure–activity connections that have not yet been thoroughly investigated for this class of compounds, three structurally related zwitterionic Schiff base derivatives are compared as corrosion inhibitors for carbon steel in 1 M H_2SO_4. Two iminium–enolate Schiff bases from substituted aromatic amines, 3-{(E)-1-[(3-chlorophenyl)iminiumyl]ethyl}-6-methyl-2-oxo-2H-pyran-4-olate and 3-{(E)-1-[(3-methylphenyl)iminiumyl]ethyl}, are among the inhibitors under investigation.-6-methyl-2-oxo-2H-pyran-4-olate and a homologue of the hydroxyl-functionalized zwitterionic Schiff base that was previously described for XC48 steel. The evaluation of how minor structural changes halogen, alkyl, and hydroxyl substituents control adsorption behavior, electrochemical responsiveness, and corrosion inhibition efficiency is given special consideration. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) are used to assess the three compounds' inhibitory efficacy, enabling a thorough examination of charge-transfer resistance, interfacial processes, and inhibition mechanisms.

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This comparative study offers insights into the logical design of effective zwitterionic Schiff base inhibitors for acidic environments by connecting molecular structure with adsorption thermodynamics and electrochemical characteristics.

II. MATERIALS AND METHODS

A. Materials

In this investigation, carbon steel specimens (XC48) were utilized. The steel samples were mechanically abraded using increasing grades of silicon carbide papers (400 to 1200 grit) prior to each experiment. They were then cleaned with distilled water, degreased with ethanol, and dried in warm air.
Analytical-grade sulfuric acid was diluted with bidistilled water to create 1 M H_2SO_4, which was the corrosive medium. Every experiment was conducted at room temperature in naturally aerated circumstances.
Three zwitterionic Schiff base compounds were examined as inhibitors: one hydroxyl-functionalized analogue, two iminium–enolate systems with aromatic rings replaced with methyl and chloro. Fresh inhibitor solutions were made by dissolving suitable concentrations of each component in the acidic medium to achieve concentrations between 100 and 600ppm.

B. Synthesis and Characterization of the Zwitterionic Schiff Bases

Following methods described in the literature [7,8], the zwitterionic Schiff base derivatives were created by condensation reactions between the suitable substituted aromatic amines and carbonyl precursors under reflux conditions. Before being used, the stable zwitterionic iminium–enolate structures that were produced by the reactions were separated, cleaned, and dried. FTIR spectroscopy and ^1H NMR were used to confirm the produced compounds' structures. Schiff base production was confirmed by FTIR spectra that showed distinctive bands linked to the azomethine (C=N) group and the enolate functionality. The suggested chemical structures were further confirmed by ^1H NMR spectra, which showed diagnostic proton signals connected to the aromatic and iminium moieties [9, 4].

C. Electrochemical measurements

A standard three-electrode cell with a platinum counter electrode and a saturated calomel reference electrode was used to perform electrochemical tests. To find corrosion parameters and inhibition efficiency, potentiodynamic polarization tests were carried out by scanning the potential around the open-circuit potential at a constant scan rate. Charge-transfer resistance and interfacial capacitance were assessed by electrochemical impedance spectroscopy (EIS) measurements at the open-circuit voltage over a broad frequency range using a small-amplitude AC perturbation. Thermodynamic adsorption parameters were determined by fitting inhibitory efficiency data to adsorption isotherm models in order to understand adsorption behavior. To guarantee that the results could be duplicated, every experiment was conducted again.

D. Adsorption Isotherm and Thermodynamic Parameters

By fitting experimental inhibition efficiencies to different adsorption isotherms, the adsorption behavior of the zwitterionic Schiff base inhibitors on the carbon steel surface was assessed. The Langmuir adsorption isotherm, which shows monolayer adsorption of inhibitor molecules on the steel surface, provided the best fit. The equilibrium adsorption constant obtained from the Langmuir model was used to compute the standard free energy of adsorption (ΔGads). The kind and strength of inhibitor–metal interactions were evaluated using the magnitude and sign of ΔGads values [10,11].

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III. RESULTS AND DISCUSSION

A. Comparative Electrochemical Performance

According to electrochemical studies, all three zwitterionic Schiff bases function as mixed-type inhibitors and successfully prevent carbon steel corrosion in 1 M H_2SO_4.. Tafel polarization experiments for the iminium–enolate derivatives revealed that the halogenated molecule had an inhibitory efficiency of around 82% at 600 ppm, whereas the alkyl-substituted analogue had a lower efficiency of about 72% in the same circumstances. Since the chloro group increases adsorption through greater molecule polarity and stronger metal–inhibitor interactions, these variations can be directly linked to substituent electronic effects.

At a lower dosage of 400 ppm, the hydroxyl-containing zwitterionic counterpart demonstrated greater inhibitory effectiveness, with efficiencies reaching 80.85%. The presence of the –OH group is responsible for this improved behavior since it increases the contact between the inhibitor molecule and the steel surface and creates new adsorption pathways through hydrogen bonding.

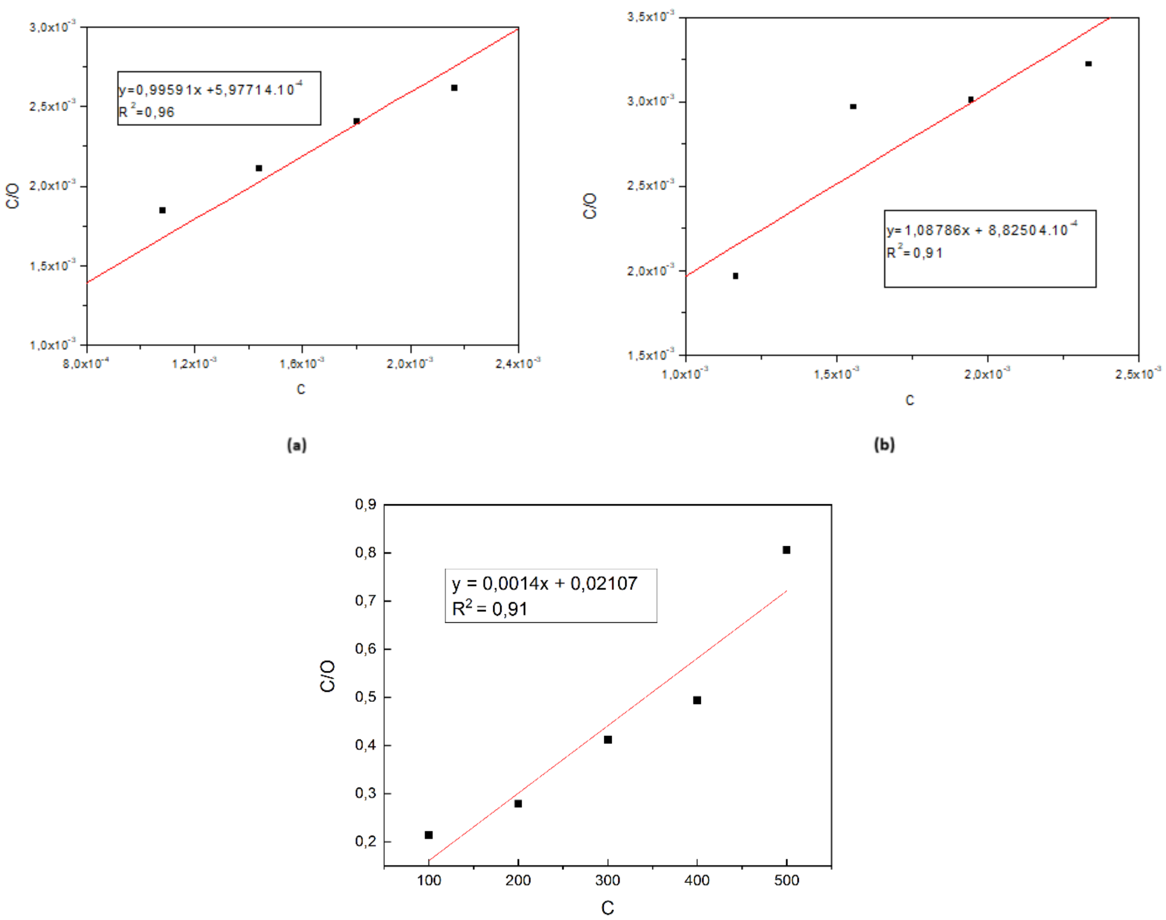
A single depressed capacitive loop characterizes the Nyquist plots of carbon steel in 1 M H_2SO_4. 4 both with and without the zwitterionic Schiff base inhibitors. The existence of a single loop over the examined frequency range suggests that charge-transfer events at the metal–solution interface are primarily responsible for controlling the corrosion process. The use of a constant phase element (CPE) in the equivalent circuit model effectively captures surface heterogeneity, roughness, and non-uniform current distribution, which are frequently blamed for the semicircle's departure from perfect capacitive behavior.

The Nyquist semicircle significantly enlarges after the inhibitors are added, indicating an increase in the charge-transfer resistance (R_ct). The development of a protective adsorbed coating on the steel surface, which prevents electron transport between the metal and the corrosive medium, is confirmed by this behavior. Concurrently, a decrease in the double-layer capacitance (C_dl) is seen, indicating either an increase in the thickness of the electrical double layer due to inhibitor adsorption or a decrease in the local dielectric constant. In comparison to the halogenated and alkyl-substituted derivatives, the hydroxyl-containing zwitterionic Schiff base has the greatest Nyquist loop, indicating stronger adsorption and higher inhibitory efficiency.

B. Adsorption Behavior and Thermodynamic Considerations

The Langmuir adsorption isotherm is obeyed by the three zwitterionic inhibitors (Fig. 1), according to adsorption experiments, suggesting monolayer adsorption with negligible lateral interactions between adsorbed species. For the halogenated and alkyl-substituted iminium–enolate derivatives, the computed standard free energy of adsorption (ΔG_{ads}) were −28 and −27 $kJ \cdot mol^{-1}$, respectively, indicating robust adsorption dominated by coupled donor–acceptor and electrostatic interactions [12].

The hydroxyl-functionalized zwitterionic Schiff base, on the other hand, showed a more negative ΔG_{ads} value (−33.254 $kJ \cdot mol^{-1}$), indicating stronger adsorption and a larger chemisorption contribution. Its greater inhibitory efficacy at lower concentrations is explained by this thermodynamic evidence, which also emphasizes the critical role of functional groups that can strengthen surface contacts.



(a) **(b)**

(c)

Fig. 1 Langmuir adsorption isotherm for the three zwitterionic inhibitors

C. Structure–Inhibition Relationship

The molecular structures of the investigated zwitterionic Schiff bases, particularly the zwitterionic iminium–enolate skeleton [13,14], the kind of aromatic substituents, and the presence of extra functional groups that can improve adsorption, have a significant impact on the inhibitory performance. Similar to other zwitterionic corrosion inhibitors in acidic conditions, zwitterionic compounds contain internal charge separation that improves electrostatic interactions with charged spots on the steel surface [15,16]. According to research on Schiff base systems, the azomethine (–C=N–) group and the aromatic π-electron system offer donor–acceptor interaction sites that promote adsorption via lone pairs and π–d orbital overlap with the metal surface [17,18]. Substituent electronic effects provide an explanation for the three inhibitors' comparative performance. For instance, halogen substituents like the 3-chlorophenyl group can improve adsorption strength and surface coverage by increasing molecular polarity and electron-withdrawing capacity [19]. Electron-withdrawing groups have been shown to enhance inhibitory efficacy by stabilizing adsorbed states in substituted aromatic Schiff bases [20]. On the other hand, electron-donating alkyl groups, such as 3-methylphenyl, offer comparatively less electron polarization, which is associated with less effective inhibition.[21].

Due to extra adsorption interactions, the hydroxyl-functionalized counterpart exhibits the highest inhibitory efficacy and the most negative free energy of adsorption (ΔG_ads). The hydroxyl group improves adsorption stability by increasing the electron density on the aromatic ring and facilitating hydrogen-bonding interactions

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with the steel surface or adsorbed water molecules [22]. For inhibitors with hydroxyl functions, these synergistic interactions (hydrogen bonding, electrostatic attraction, and π-electron donation) have been linked to increased inhibition.[23].

This view is further supported by electrochemical impedance spectroscopy results, which show that the inhibitor with the most advantageous structural characteristics increases charge-transfer resistance the greatest, indicating better adsorption and a more compact protective layer. This finding is consistent with general patterns observed for mixed-type organic inhibitors, wherein adsorption-promoting structural characteristics are associated with reduced double-layer capacitance and greater Rct [24,25].

Overall, these findings show that specific structural changes, such as the addition of electron-donating or electron-withdrawing substituents and functional groups that can form hydrogen bonds, have a substantial impact on interfacial properties, corrosion inhibition efficiency, and adsorption strength. The rational design of zwitterionic corrosion inhibitors tailored for acidic environments is based on these structure–activity correlations.

IV. CONCLUSION

This study establishes a strong structure–inhibition link substantiated by electrochemical and thermodynamic investigations and shows the exceptional corrosion inhibition performance of three structurally related zwitterionic Schiff base derivatives for carbon steel in 1.0 M H_2SO_4. Electrochemical impedance spectroscopy and potentiodynamic polarization consistently show that all substances act as mixed-type inhibitors, strongly inhibiting both cathodic hydrogen evolution and anodic metal dissolution processes. Negative values of the standard free energy of adsorption indicate a strong and spontaneous interaction at the metal/solution interface, and the inhibitors' adsorption on the steel surface follows the Langmuir isotherm. The inhibitors can be classified as follows by comparing their inhibition efficiency, charge-transfer resistance, and adsorption free energies: hydroxy derivative > chloro derivative > methyl derivative.

The synergistic contribution of the –OH group, which improves adsorption through hydrogen bonding and increases surface coverage, is responsible for the hydroxyl-containing inhibitor's improved efficacy. Because of the halogen substituent's electron-withdrawing function, which strengthens interfacial contacts, the chlorinated derivative has intermediate efficiency, while the methyl-substituted counterpart has somewhat lower adsorption and inhibition effectiveness.

Overall, this work underlines the critical importance of molecular design in controlling inhibition performance and highlights zwitterionic Schiff bases as a very promising family of corrosion inhibitors. The knowledge acquired offers a logical framework for the molecular design of sophisticated zwitterionic inhibitors, providing insightful viewpoints for their use in harsh acidic environments and aiding in the creation of effective, structure-guided corrosion prevention techniques.

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