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Pyridinium salts as corrosion inhibitors for mild steel in acidic solution: Theoretical and experimental approaches

ABSTRACT

New pyridinium salts, namely: 1-benzyl-4-(2-(4-nitrobenzylidene)hydrazineyl)pyridin-1-ium bromide, R1; 1-butyl-4-(2-(4-nitrobenzylidene)hydrazineyl)pyridin-1-ium bromide, R2; 4-(2-(4-nitrobenzylidene)hydrazineyl)-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide, R3 were successfully prepared as organic corrosion inhibitors for mild steel. The weight loss method was used to evaluate these salts in 1M H₂SO₄ which was carried out for 24 hours at room temperature. Across a variety of prepared salt concentrations, the inhibitory efficiency results for all these salts (R1-R3) as inhibitors were high. The rate of corrosion decreased with increasing inhibitor concentration, while the degree of surface coverage and inhibition efficiency increased. The physisorption process for these prepared compounds (R1, R2, and R3) was predicted by the calculated data of adsorption results.

For these organic inhibitor salts, semi-empirical molecular orbitals level, and the molecular mechanics approach was run to exam the correlation between experimental and theoretical data. In addition, the nature of the interaction between the organic inhibitor molecular salt and the iron metal surface was obtained by performing theoretical simulations.

Keywords: Pyridinium salts, physisorption, molecular simulation, corrosion inhibitors

1. INTRODUCTION

The corrosion process refers to the degradation of materials resulting from their chemical interaction with the surrounding environment. The majority of metals experience corrosion when they come into contact with water or moisture present in the air. This interaction can involve acids, bases, salts, oils, harsh metal cleaners, and various other solid and liquid substances [1]. Iron is a commonly utilized material within the construction sector, serving numerous purposes. Consequently, an

extensive analysis and evaluation of various corrosion inhibitors have been performed to reduce and avert corrosion reactions on the surface of iron [2-5]. Corrosion inhibitors work by minimizing and preventing corrosion reactions through the introduction of a small concentration into the corrosive environment [6]. This inhibition can be accomplished by creating a monomolecular film that adsorbs onto the surface [7], effectively blocking direct contact between the metal and the corrosive surroundings [8, 9].

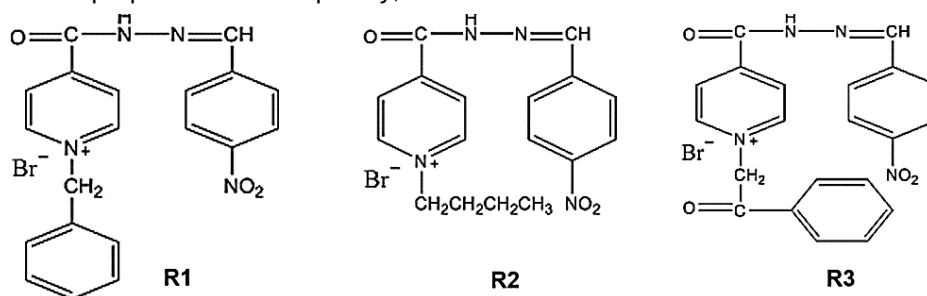


Figure 1. The formula of prepared inhibitor molecules

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This inhibition can be accomplished by creating a monomolecular film that adsorbs onto the surface [7], effectively blocking direct contact between the metal and the corrosive surroundings [8, 9].

Heteroatoms such as nitrogen (N), phosphorus (P), and oxygen (O) found in organic chemical compounds have been shown to significantly enhance the corrosion inhibition process [10], thereby serving as a protective barrier against corrosion. Numerous research studies have been conducted utilizing computational design systems for various organic molecules aimed at preventing metal corrosion [11, 12]. This study's objective was to develop an understanding of how organic compounds interact when situated near metal surfaces in acidic environments. Computational methods play a crucial role in examining the reduction of corrosion processes, as they effectively contribute to the development of inhibitors and their application in industrial settings. In this paper, quantum chemical calculations will be executed on three compound salts, which are illustrated in Figure 1. The molecular parameters calculated were correlated to derive the inhibitory

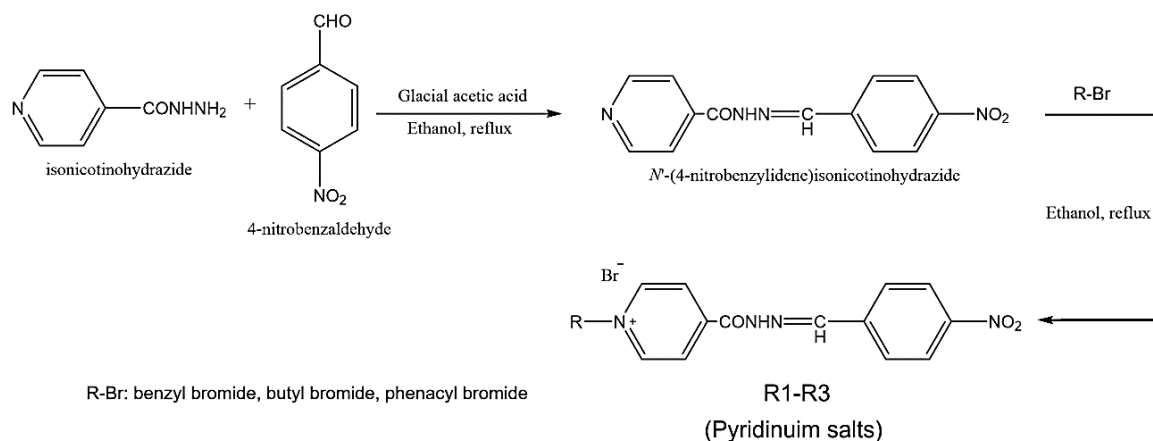
activities of these pyridinium salts.

2. EXPERIMENTAL PART

All reagents and solvents were employed as received, without any further purification. ^1H NMR spectra (using DMSO-d_6 as a solvent) and FTIR spectroscopy (in the range $4000\text{--}400\text{cm}^{-1}$) for all synthesized salts was recorded by Bruker Company.

2.1. General procedure of prepared pyridinium salts

New pyridinium salts, namely: 1-benzyl-4-(2-(4-nitrobenzylidene)hydrazineyl)pyridin-1-ium bromide, R1; 1-butyl-4-(2-(4-nitrobenzylidene)hydrazineyl)pyridin-1-ium bromide, R2; 4-(2-(4-nitrobenzylidene)hydrazineyl)-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide, R3 were synthesized according to Scheme 1 [13].



Scheme 1: The pyridinium salts synthesis steps (R1-R3)

- 1-benzyl-4-(2-(4-nitrobenzylidene)hydrazineyl)pyridin-1-ium bromide (R1)

a) Schiff base compound. A mixture of (0.01 mol) 4-nitrobenzaldehyde with (1.37 gm, 0.01 mol) isonicotinic hydrazide in 20 mL of absolute ethanol, with (2-3) drops of glacial acetic acid. The reaction mixture was refluxed for 6 h. Finally, the precipitate of the Schiff base compound was formed, collected by filtration, dried and recrystallized with ethanol. Yellow, 90 % yield, mp $255\text{--}257^\circ\text{C}$, FTIR, $\nu\text{ cm}^{-1}$, 3341, 3102, 1677, 1635, 1556, 1503, 1411.

b) Pyridinium salt. A mixture of (0.01 mol) Schiff's base with (0.01 mol) of benzyl bromide in 10 mL of ethanol was allowed to stand overnight at room temperature. The mixture was then heated at reflux for 48 hours. Then the product was filtered, washed with ethanol and dried. Brown, 78 % yield, mp gummy, FTIR, $\nu(\text{cm}^{-1})$, 3401, 3052, 2950, 2870, 1677, 1635, 1556, 1490, 1406. ^1H NMR, δ (ppm), 4H of pyridine-ring (9.0-9.4); 1H of $\text{N}=\text{CH}-$ (8.5); 9H

of phenyl-rings (7.1-8.2); 2H of $-\text{N}^+-\text{CH}_2$ group (6.0); 1H of O-H (3.4, tautomerism of $-\text{CO}-\text{NH}-$ moiety)

- 1-butyl-4-(2-(4-nitrobenzylidene)hydrazineyl)pyridin-1-ium bromide (R2)

A mixture of (0.01 mol) Schiff's base with (0.01 mol) of butyl bromide in 10 mL of ethanol was allowed to stand overnight at room temperature. The mixture was then heated at the reflux for 48 hours. Then the product was filtered, washed with ethanol and dried. Yellow, 81 % yield, mp $220\text{--}222^\circ\text{C}$, FTIR, $\nu\text{ cm}^{-1}$, 3425, 3064, 2931, 2804, 1684, 1641, 1551, 1502, 1411. ^1H NMR, δ (ppm), 1H of N-H ($-\text{CO}-\text{NH}-$ moiety) (12.5); 4H of pyridine-ring (8.7-9.3); 1H of $\text{N}=\text{CH}-$ (8.5); 4H of phenyl-rings (7.7-8.3), 2H of $-\text{N}^+-\text{CH}_2$ group (4.6); 7H of aliphatic chain (0.9-1.9)

- 4-(2-(4-nitrobenzylidene)hydrazineyl)-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide (R3)

A mixture of (0.01 mol) Schiff's base with (0.01 mol) of phenacyl bromide in 10 mL of ethanol was allowed to stand overnight at room temperature. The mixture was then heated at the reflux for 48 hours. Then the product was filtered, washed with ethanol and dried. Yellow, 88 % yield, mp 240-243°C, FTIR, ν cm^{-1} , 3361, 3052, 2976, 2897, 1680, 1643, 1593, 1512, 1449. ^1H NMR, δ (ppm), 1H of N-H (-CO-NH- moiety) (12.5); 4H of pyridine-ring (8.6-9.2); 1H of N=CH- (8.5); 9H of phenyl-rings (7.7-8.3), 2H of -N+-CH₂ group (6.5).

2.2. Preparation of aggressive solution

A solution of 98% H₂SO₄ was diluted with a distilled water to obtain a 1M H₂SO₄ solution. The concentrations of prepared inhibitors (R1-R3) have proven effective as a corrosion inhibitor were range from 5×10^{-4} to 1×10^{-2} M in the presence a 1M solution of H₂SO₄.

2.3. Weight loss measurements

The mild steel specimen had the following composition: 0.288 % Mn, 0.0154 % S, 0.03 % C, 0.0199 % Cr, 0.065 % Cu, 0.002% P, and 0.0005 % V, 0.002 % Mo, remain Fe. The mild steel sheet was mechanically press-cut into disc shape with diameter (2.5 cm). These disc shapes were polished with emery paper up to 2000 grade to obtain a smooth surface. Then, they were cleaned with distilled water, alcohol, and finally acetone. Initially, the specimens were dried in a desiccator before corrosion tests. In the first step, electronic balance was used to weigh the steel disc. In the presence and absence of the known concentration of prepared organic inhibitor, the mild steel disc was immersed in 1M sulfuric acid. After that, it was washed with a sufficient amount of water and acetone after being exposed to room temperature (25°C) for 24 hours, and then it was re-weighed after drying and stored in a desiccator. Weight loss measurements were performed in triplicate according to the ASTM test [14] for the purpose of ensuring the accuracy of the results using the weight loss method, and thus the average corrosion rate was calculated from the measured weight loss in ($\text{mg cm}^{-2} \text{h}^{-1}$) with relative standard deviation (%RSD between %1.01-0.92 for raw triplicate data). Equation (1) used to calculate the corrosion rate of mild steel was as a following [15]:

$$W = \frac{\Delta m}{St} \quad (1)$$

Where W = corrosion rate ($\text{mg cm}^{-2} \text{h}^{-1}$), Δm =

difference of weight loss (mg) prior to and after immersion of specimen, S = sample area (cm^2) and t = immersion time (hrs). Equation (2) was used to calculate the inhibition efficiency (IE%) as a following [16]:

$$IE\% = \frac{W_{\text{corr}} - W_{\text{corr(inh)}}}{W_{\text{corr}}} \times 100 \quad (2)$$

Where W_{corr} and $W_{\text{corr(inh)}}$: corrosion rates in both absence and presence of the inhibitor respectively.

2.4. Theoretical Calculations

Correlation has been studied between experimental data via inhibition efficiencies for mild steel corrosion process in acidic environment and theoretical calculations [17, 18]. While the relationship between molecular reactivity and inhibitory efficacy is established from experimental data, the study's explicit goal is to comprehend the electronic form of some prepared chemical inhibitors using theoretical calculations. Molecular mechanics was used for the purpose of theoretical calculations at MM+ level, while the PM3 method was used for semi-empirical calculations of organic inhibitor molecules in the gas phase and without restrictions at a temperature of 25°C. So, the HyperChem 7.52 Program [19, 20] which has a full geometry improving was used for this purpose. To understand the inhibition efficiency of the synthesized inhibitors, simple quantum calculations using the PM3 method were carried out to estimate the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) to analyze calculated quantum parameters. Using the PM3 method to estimate parameters such as the frontier orbital energy gap (ΔE), molecular dipole moment (μ), polarizability (α), electron affinity (A), ionization potential (I), electronegativity (χ), global hardness (η), softness (σ), the fraction of electron transferred (ΔN), electrophilicity index (ω), nucleophilicity index (ϵ) and back-donation ($\Delta E_{\text{back-donation}}$) (see Table 1).

According to Koopman's theorem and Fukui indices [21], These calculated quantum parameters were used to evaluate the properties and reactivity of the synthesized pyridinium salts (R1-R3). They also help correlate quantum calculated parameters with experimental data, which is obtained by loss weight method for the corrosion process [22].

Table 1. Quantum approximated calculated parameters as following relationships

$I = -E_{\text{HOMO}}$	$A = -E_{\text{LUMO}}$	$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$	$\chi = \frac{I + A}{2}$
$\eta = \frac{I - A}{2}$	$\omega = \frac{\chi^2}{2\eta}$	$\epsilon = \frac{1}{\omega}$	$\Delta N = \frac{\chi_{\text{Fe}} - \eta_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})}$
$\sigma = \frac{1}{\eta}$	$\Delta E_{\text{back-donation}} = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{8} = -\frac{\eta}{4}$		

where χ_{Fe} and χ_{inh} represent the absolute electronegativities of the inhibitor molecule and the metal, respectively. The absolute hardness of iron is denoted by η_{Fe} , whereas the inhibitor molecule is represented by η_{inh} . Since they are softer than the metallic atoms, it is assumed that for a metallic bulk ($I = A$), $\chi_{\text{Fe}} = 7.0$ eV and $\eta_{\text{Fe}} = 0$ for the calculation of the electron transmitted (ΔN) [23]. Thus, the electron transport is driven by the difference in electronegativity, and the total hardness characteristics serve as a resistance [24].

The MM+ force field developed by Hyperchem, which is derived from Allinger's MM2, is explained and compared to other MM2 versions in terms of the conjugation process, the rotation, and structural energy differences. It may also be used to quantify the forces that exist between and within molecules [25]. At atmospheric pressure, iron can be found in two distinct crystal structures: the body centered cubic (bcc), which is stable in the ground state, and the face centered cubic (fcc) [26].

A model metallic surface was prepared using an iron crystal surface obtained by constructing the crystal shape of iron and the surface had optimized to smallest energy utilizing the Hyperchem's MM+ force field. Unit cells (11×3) of Fe crystal surface were built, and from the optimized crystal surface as an adsorbance surface for inhibitor molecules. The synthesized inhibitor compound was allowed to adsorb and interact with surface particles of the metal crystal surface by adsorption locator module (adsorption locator module identifies possible adsorption sites by carrying Hyperchem's MM+ force field searches of the configurational space of the substrate-adsorbate). A suitable distance between the adsorbate and the chosen iron crystal surface for optimization by Hyperchem's MM+ force field was maintained.

The theoretical methodology relies on semi-empirical quantum mechanics (PM3) and classical molecular mechanics (MM+) to approximate the interaction energy and geometry of inhibitor adsorption on iron. In this computational setup, designated (Fe^{2+}) typically refers to a simplified model where the metal surface is approximated using an iron cation as cluster of charged iron centers of metallic lattice. In acidic or aqueous corrosive media, iron undergoes oxidation (Fe^{2+}). Modeling (Fe^{2+}) isolates the electrostatic and coordination interactions between electron-rich organic donor atoms (N, O, S, and π -systems) and the oxidized iron surface sites. It simplifies the calculation to evaluate the formation of surface complexes or coordinate bonds between the inhibitor's highest occupied molecular orbital

(HOMO) and the empty d-orbitals or positive charge of the iron ion. While PM3 and MM+ offer low computational costs, several important approximations constrain these results, as PM3 relies on heavily parameterized integral approximations that often struggle with transition metals like iron due to complex d-orbital correlations. MM+ relies on classical force fields that lack electronic structure representation entirely, making it unable to model dynamic charge-transfer processes or bond breaking/making during chemisorption. These calculations are generally performed in the gas phase, neglecting explicit water molecules, counterions (Cl^- , SO_4^{2-}) pH effects, and competitive adsorption with solvent molecules.

3. RESULTS AND DISCUSSION

3.1. Experimental Investigation

Some pyridinium salts, namely: 1-benzyl-4-(2-(4-nitrobenzylidene) hydrazineyl) pyridin-1-ium bromide, R1; 1-butyl-4-(2-(4-nitrobenzylidene) hydrazineyl)pyridin-1-ium bromide, R2; 4-(2-(4-nitrobenzylidene) hydrazineyl)-1-(2-oxo-2-phenylethyl) pyridin-1-ium bromide, R3 were synthesized, and their structures were confirmed.

3.2. Study of corrosion

After immersion of mild steel for 24 h at room temperature, corrosion degradation was determined. Measurements of weight loss method was used to obtain the rate of corrosion and effectiveness of inhibition by using different concentrations of inhibitor compounds (R1-R3) which are mentioned in Table(2).

Table 2 demonstrates that when the concentration of the inhibitor is raised, the corrosion efficiency increases and reaches high inhibition efficiencies at 10^{-2} M. In contrast, the inhibition efficiency follows the order ($R3 > R1 > R2$) could be comparable. The effects of the carbon chain length in the organic molecular structure on inhibition efficiency may be explained by values of the inhibition ability [27], where the chain fragments in R1 and R3 may facilitate the adsorption of the entire organic molecule to adsorb on the metal surface rather than with R2 molecule. Basic adsorption information provides insight into the nature of the interactions occurring at the surface of metal and chemical molecular compound. Therefore, the values of plane coverage degree (θ), with various inhibitor of concentration was achieved by weight loss tests with 1 M sulfuric acid by the surface coverage degree, ($\theta = \text{IE}(\%)/100$) (see Table 2) at room temperature, the Equ. (3), Langmuir Adsorption Isotherm is showing the

relationship between surface coverage degree and concentrations inhibitor to calculate [28]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

Where C is concentration of inhibitor (M), K_{ads} is the value of equilibrium constant (M^{-1}).

Table 2. Weight loss at room temperature for 24 hour period is measured together with the rate of corrosion, capacity of inhibition (IE%), coverage of surface (θ), and ΔG°_{ads} for mild steel tested with 1 M sulfuric acid

Concentration (M)	The rate of corrosion ($mg.cm^{-2}.h^{-1}$)	IE%	θ	ΔG°_{ads} ($kJ.mol^{-1}$)
Blank	0.3440			
R1				
5×10^{-4}	0.1789	47.99	0.4799	-29.58 ($R^2=0.9992$)
1×10^{-3}	0.0721	79.04	0.7904	
5×10^{-3}	0.0521	84.85	0.8485	
1×10^{-2}	0.0437	87.30	0.8730	
R2				
5×10^{-4}	0.2658	22.73	0.2273	-25.65 ($R^2=0.9975$)
1×10^{-3}	0.2208	35.81	0.3581	
5×10^{-3}	0.1511	56.08	0.5608	
1×10^{-2}	0.1168	66.05	0.6605	
R3				
5×10^{-4}	0.0496	85.58	0.8558	-33.06 ($R^2=0.9999$)
1×10^{-3}	0.0377	89.04	0.8904	
5×10^{-3}	0.0276	91.98	0.9198	
1×10^{-2}	0.0220	93.60	0.9360	

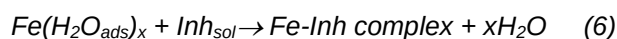
The Langmuir isotherm model describes monolayer adsorption onto a homogeneous metal surface with a fixed number of identical binding sites. Its linear expression. As showing in Table 2, The value of (R^2) indicates the proportion of total variation in surface coverage (θ) that is directly explained by changes in the inhibitor concentration (C) under the assumptions of the model. Because all three inhibitors have ($R^2 > 0.99$), the corrosion inhibition process strongly obeys the Langmuir adsorption isotherm. The high (R^2) values confirm that inhibitor molecules form a single layer (monolayer) on active site locations on the mild steel surface.

The values of K_{ads} were computed from the crossings of the straight line of C/θ vs concentration, in accordance with the Langmuir isotherm. Equation (4) was used to calculate the values of ΔG°_{ads} [29]: (the molar concentration of water is 55.5 M).

$$K_{ads} = \frac{1}{55.5} \exp \left(-\frac{\Delta G^{\circ}_{ads}}{RT} \right) \quad (4)$$

Table 2 shows the standard Gibbs free energy of adsorption values, which are negative, indicating that the adsorption of compounds R1–R3 onto the mild steel surface is a spontaneous process in 24 hrs of dipping at room temperature, and the interaction between the metal surface and organic

molecules (R1-R3) was seen by using this method to present a clear image. All three inhibitors operate via a mixed adsorption mechanism (both physical electrostatic attraction and chemical coordination), as all values fall squarely between (-20 kJ/mol) and (-40 kJ/mol). Among them, R3 exhibits the strongest binding affinity to the mild steel surface, which directly explains why it achieves the lowest corrosion rate and highest inhibition efficiency. Organic compounds move toward the metal surface during a corrosion reaction, causing molecule electrons to interfere with the surface atoms' unoccupied orbitals [30]. This process is also referred to as the retro-donation mechanism [31]. Equations (5,6) [32] below illustrate how the presence of donor atoms in the inhibitor complicates the adsorption process between the inhibitor molecules and the metal:



Furthermore, at low concentrations of the produced organic inhibitor, the number of metal complexes on the metal surface may be reduced. Thus, it is evident that as the concentration of organic inhibitors increases, so does the inhibition efficiency. The process by which adsorption compounds act through (N and S) atoms that

contain organic molecule inhibitors is known as the adsorption inhibitor mechanism. Functional groups inside molecules are said to play a role in the electron density distribution of molecules, which can significantly affect the adsorption process on metal surfaces [33]. Organic inhibitors (R1–R3) that the active anode sites were accepting by adsorbing with the metal surface were utilized in thin film complexes to prevent or stop the loss of metal atoms from the surface that can result from the reaction of electrochemical dissolutions. Through the interaction between the organic molecules and the charged centers on the electrode metal surface and the metal surface itself, physical adsorption takes place both physically and electrostatically, as indicated by the values of the $\Delta G^{\circ}_{\text{ads}}$ for (R1–R3) listed in Table 2 [34]. The organic inhibitor (R3) was shown the value $\Delta G^{\circ}_{\text{ads}} = -33 \text{ kJ/mol}$, that's was clear by confirming the values of IE% (85–93) at the various concentrations and listed in Table 2. At the high concentration of inhibitor, IE% of (R1–R3) are compatible with the values of $\Delta G^{\circ}_{\text{ads}}$, follows the order $R3 > R1 > R2$. We think this is

because of the spatial geometry of (R1–R3) and the molecular structure of a different carbon chain on the N atom of the pyridinium ring, which results in a different intensity of electron density surrounding the organic molecule. Consequently, it is anticipated that the interaction between molecule (R2) and the surface metal will improve when the regular distributions of electron densities of molecules with the metal are compared to molecules (R3 and R1).

3.3. Theoretical Investigation,

Semi-empirical calculations employing PM3 level were used to correlate the experimental inhibitory efficacy of the proposed inhibitors with their molecular structure model. More stable energetic conformations were employed in all theoretical calculations for the proposed inhibitors of the pyridinium salts (R1–R3). These conformations are proven to be planar across the entire molecular model of the inhibitors that are proposed and caused by molecular systems (see Fig. 2).

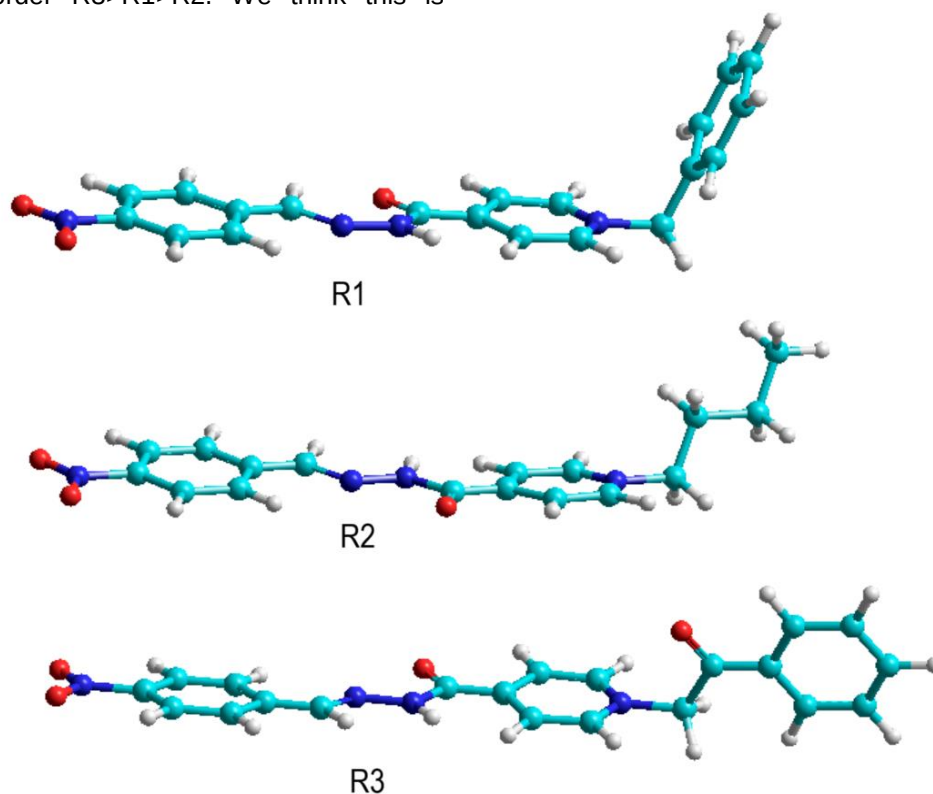


Figure 2. The suggested pyridinium salt (R1–R3) inhibitors' conformations that are energetically stable using the PM3 approach

The HOMO and LUMO isosurface maps for the suggested inhibitors of (R1–R3) are displayed in Fig. 3. For all compounds, the N and O atoms found in the suggested inhibitors have the full concentration of the HOMO and LUMO electronic

densities. With the exception of the N atom of the pyridinium ring, the electronic density of O and N atoms in the molecular system thus serves as a donor for the intermolecular interaction with the ambient metal surface (Fe^0 and Fe^{II}).

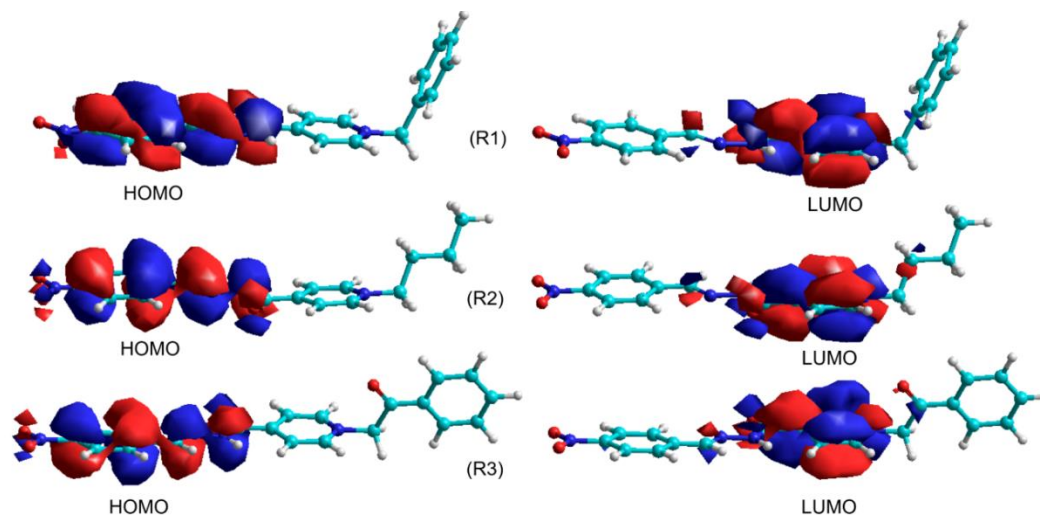


Figure 3. The suggested inhibitors of the pyridinium salts (R1–R3) and their molecular orbital density boundary distributions (HOMO and LUMO) were determined using the PM3 method

Accordingly, the pyridinium salts (R1), (R2), and (R3) have computed HOMO energies of --11.4737, -11.5263, and -11.4142 eV, respectively (see Table 3). The values of the maximum IE% and $\Delta G^{\circ}_{\text{ads}}$, as well as the HOMO energies, are obviously close together (see Table 2). In other words, there is an intriguing congruence between experimental and theoretical evidence. According to Table 3, the LUMO energy for (R1–R3) is -5.7830, -5.9041, and -5.7032 eV, respectively. Accordingly, by comparing their LUMO energies to those of other inhibitors, the inhibitors with the lowest LUMO energy can easily receive electrons from the corroding surface metal's d-orbital. Another crucial quantum parameter that must be taken into account is the energy band gap between HOMO-LUMO energy levels; the lower the band gap, the higher the corrosion inhibition efficiency

[35]. Table 3 demonstrates that (R3) has superior corrosion inhibition efficacy with the lowest band gap energy compared to (R1 and R2). According to this, the structural molecule of inhibitor (R3) can be very important in the adsorption process on the metal surface because the carbon chain with the N atom of the pyridinium ring allows overall molecules to be flexible enough to position themselves toward the active areas on the metal surface.

Furthermore, the calculated dipole moment is an important expression of non-uniform distribution of charges on various atoms in the molecule, is to measure interactions of molecules in a particular chemical environment. Table 3 shows the dipole moments of the pyridinium salts (R1–R3) are in range (24–27 D) that values indicated that the feature of salt applies to these pyridinium salts.

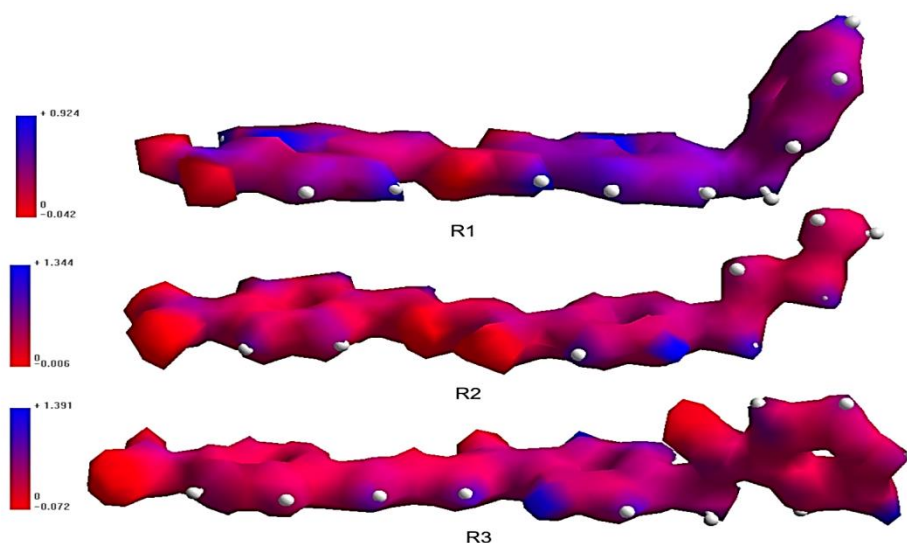


Figure 4. Maps of electrostatic potential that use the PM3 approach to show the different inhibitors' magnitudes (R1–R3)

The impact of the dipole moment on the corrosion inhibition properties is a topic of significant debate. Considerable dipole moment values, according to some researchers, have to make the organic molecules orientate on metal surfaces, whereas high values suggest potent corrosion-inhibition capabilities [36]. Therefore, as Tables (2,3) demonstrate, a molecule's corrosion inhibition efficiency increases as the dipole moment's magnitude decreases the electrostatic potential maps in Figure 4 show the different calculated dipole moment magnitudes for the suggested inhibitors (R1-R3). Strong inhibitor polarization values are associated with strong inhibition efficiency, as Table 3 shows that the compounds' polarizability order is $R3 > R1 > R2$. Strong corrosion inhibitor adsorption onto the metal surface and, consequently, great inhibition efficiency are made possible by high polarizability values [37]. Since polarizability (α) is inversely proportional to the third power of the hardness values, the qualitative definition of hardness and polarizability are closely related [38]. Consequently, as a molecule's softness increases, it becomes more polarizable (see Table 3). Because a smaller energy gap often makes it easier for the molecule to polarize, this lowers the LUMO–HOMO energy gap and increases the inhibitor's efficiency [39]. Electrostatic potential maps that show the different calculated polarizability magnitudes are shown in Figure 4.

The quantity of electrons transported (ΔN) indicates a molecule's propensity to transfer electrons to an electron-deficient species; the higher the value of ΔN , the more likely a molecule is to do so. In order to increase corrosion inhibition efficiency, it seems sense that an organic corrosion inhibitor with a larger ΔN would have a higher propensity to interact with the metal's surface [40]. Table 3 demonstrates that (R1, R3) transmits more electrons than (R2). This is in good agreement with the experiment's results. The ionization potential (I) of an atom or molecule is a key measure of its chemical reactivity. Strong reactivity of the atoms and molecules is indicated by a small ionization potential, whereas considerable stability and chemical inertness are indicated by a high ionization potential [41]. Compound (R3) with low ionization potential ($I = 11.4242$ eV) indicates its high inhibitory effectiveness. This is in good agreement with the experiment's results.

Absolute electronegativity (χ) is the chemical property that describes a molecule's ability to attract electrons into itself in a covalent bond.

Inhibitors with lower electronegativity values donate electrons more readily, making them more reactive toward the metal surface. This is due to the fact that corrosion inhibitors with low electronegativity values will be more reactive or easier to donate electrons [42,43].

According to Sanderson's electronegativity equalization theory, a molecule (R3) with a low electronegativity quickly achieves fair distribution. High responsiveness is therefore anticipated, indicating good inhibitory efficiency [44]. Table 3 shows that the molecules (R2) have a high electronegativity. As can be observed for (R2), the largest rise in electronegativity thus indicates a lesser adsorption process between the metal and inhibitor. This aligns with the experiment's results. Understanding absolute hardness (η) and softness (σ) is necessary to measure the stability and reactivity of molecules [45]. It is evident that chemical hardness basically means the ability of atoms, ions, or molecules to withstand deformation or polarization of their electron fields under modest perturbations from chemical reactions. A soft molecule has a smaller energy gap than a hard molecule [46].

In the current investigation, the salt (R3) has low hardness value (2.8516 eV) when compared to other suggested pyridinium salts. In general, a high inhibition efficiency is predicted for the inhibitor with low global hardness value (and thus the large global softness value) [47].

Adsorption tends to occur at the molecular site with the highest local softness (σ), facilitating electron transfer [48]. The pyridinium salt (R3) has a high level of inhibitory effectiveness with a softness value of 0.3506 eV^{-1} . This aligns with the findings of the experiment. Considering the stabilization energy, the ability of chemical species to acquire additional charge from the environment, and the global electrophilicity index (ω), which measures a molecule's propensity to be electrophilic [49]. We discover that the inhibitor (R3) has a higher inhibition efficiency and a good value for free energy adsorption because it has the lowest electrophilicity index value (12.8445 eV) compared to the other inhibitors (R1 and R2). The experimental data and this finding agree well. The electrophilicity index (ω) and the nucleophilicity index (ϵ) are two important considerations when evaluating corrosion inhibitors.

The ability of inhibitor molecules to supply

electrons is represented by (ϵ), while the ability to acquire electrons is represented by (ω). When the (ω) value decreases, the inhibitory activity decreases, and when the (ϵ) value increases, it increases [50]. The value of (ω) has decreased and the value of (ϵ) has increased in our molecular research. According to the (ϵ and ω) tests, our compounds (R1–R3) have the strongest inhibitory activity.

The inhibitor potency and center activity are further examined using back-donation ($\Delta E_{\text{back-donation}}$) [51]. If $\eta > 0$ and $\Delta E_{\text{back-donation}} < 0$, this kind of activity would suggest an effective inhibitory process. This would suggest a charge transfer to the molecule and a subsequent donation back to the metal atom's vacant d-orbital [52].

$\Delta E_{\text{back-donation}}$ has high advantageous for R3 and the experimental data and this finding agree well.

The vdW volume, as well as, surface area were calculated with Hyperchem, based on Quantitative Structure Activity Relationships (QSAR) which listed below in Table 3, demonstrated that R1 (1034 Å³) has comparatively greater volume than R2 (980 Å³) and R3 (1085 Å³). Thus, R3 offers a sizable adsorption contact area, which improves inhibitor activity.

Table 3. Quantum approximated chemical parameters of the studied pyridinium salt derivatives as corrosion inhibitors by using PM3 method

Inhibitor	R1	R2	R3
E_{HOMO} , eV	-11.4737	-11.5263	-11.4142
E_{LUMO} , eV	-5.7830	-5.9041	-5.7032
ΔE , eV	5.6907	5.6222	5.7110
I , eV	11.4737	11.5263	11.4142
A , eV	5.7830	5.9041	5.7032
χ , eV	8.6283	8.7152	8.5587
η , eV	2.8453	2.9520	2.8516
σ , eV ⁻¹	0.3514	0.3387	0.3506
ΔN	0.7323	0.6864	0.7280
ω , eV	13.0830	12.8643	12.8445
ϵ , eV ⁻¹	0.0764	0.0777	0.0778
$\Delta E_{\text{back-donation}}$, eV	-0.7110	-0.7380	-0.7129
VdW, Å ³ (surface area, Å ²)	1034.20 (549.88)	980.67 (584.71)	1085.08 (586.05)
Dipole moment, (D)	24.60	27.00	24.20
Polarizability, a.u.	39.21	35.05	41.13

In conclusion, the diverse molecule systems exhibit varying values of quantum approximated chemical parameters, which may indicate that the inhibitor molecule and the metal surface are interacting in different ways.

3.4. Molecular mechanics investigation

Figure 5 shows the small energy adsorption patterns of the three inhibitors adsorbed on the Fe (001) surface (Fe⁰). As illustrated in Fig. 5, the inhibitors under investigation adsorb on the surface of Fe (001) at the electrons of the nitrogen, oxygen, and benzene rings. When inhibitor molecules are adsorbed on the iron surface in a nearly flat form to promote coverage and contact with the surface, the adsorbate/substrate system interaction is strengthened [53,54]. Given that the adsorption energy (E_{ads}) can be used to characterize the potency of corrosion inhibitors absorbed on iron surfaces, it will be very appealing to investigate the adsorption energies of inhibitors absorbed on iron surfaces while accounting for inhibition performance. The adsorption energy in a solution can be calculated by following equation [55].

$$E_{\text{ads}} = E_{\text{total/complex(Fe-Inh)}} - (E_{\text{total/Fe}} + E_{\text{total/Inh}}) \quad (7)$$

The adsorption energies in the current investigation were calculated using the average adsorption energy of the obtained molecular model optimization. According to Table 4, the E_{ads} obtained for R1, R2, and R3 are -51, 52, and -53 kJ/mol, respectively. Spontaneous adsorption is anticipated since the adsorption energies are demonstrated to be negative [56]. Essentially, the stronger the contact between the organic molecule and the metal surface, has the bigger the absolute value of E_{ads} [57].

With greater absolute values of E_{ads} than R1 and R2, R3 demonstrates a definite stronger inhibition of corrosion for mild steel. These results align with experimental evidence. Figure 6 compares the relative adsorption energy for complex formation with that of each individual component (refer to Table 4). Correlation between the electrochemical values, or " $\Delta G^{\circ}_{\text{ads}}$," measured and the theoretical E_{ads} values, which are in the order R3>R1>R2. That's due to, R3 and R2 are larger molecules than R2, and because the carbon chain may have a significant impact on how the molecular system is oriented toward the metal surface, they are able to cover a greater area of the metal surface, which results in high IE%, G_{ads} , and E_{ads} values.

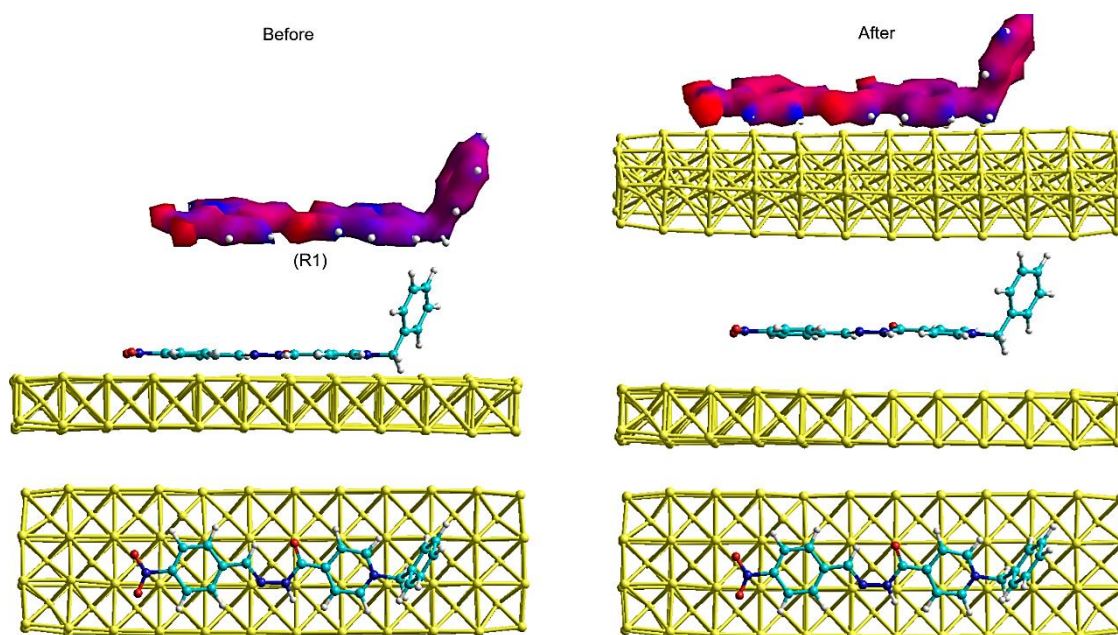


Figure 5. Side and top views of the more stable adsorption configurations and electrostatic potential maps for R1 inhibitor on Fe (001) surface (Fe^0) (before and after simulation)

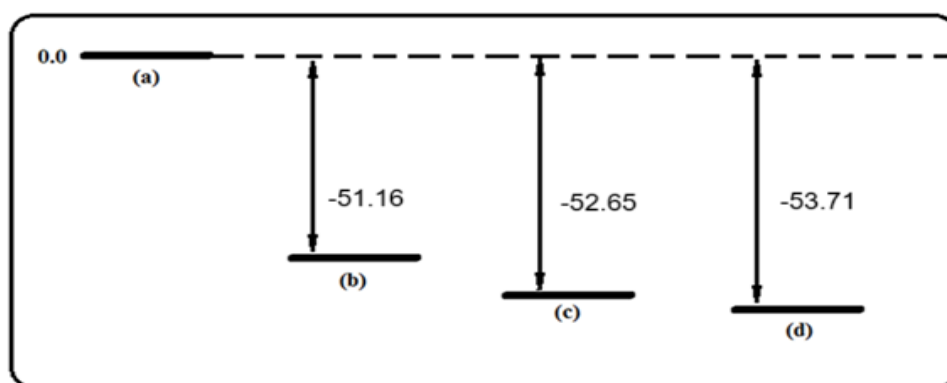


Figure 6. Diagram of proportional adsorption energy for the formation of complexes. (a) (Inh + Fe metal), (b) for complex (Fe-InhR1), (c) for complex (Fe-InhR2) and (d) for complex (Fe-InhR3); energies are in kJ mol^{-1}

Table 4. Quantum chemical properties of the proposed inhibitors with metal surface using MM+ method were computed

Component	Total energy, (kJ/mol)	E_{ads} , (kJ/mol)
R1	64.69	-51.18
R2	75.47	-52.65
R3	99.35	-53.71
Fe^0	21133.73	
Complex(Fe-InhR1)	21147.24	
Complex(Fe-InhR2)	21156.57	
Complex(Fe-InhR3)	21179.37	

To determine the stable conformations of the three inhibitors for minimal energy adsorption (R1-R3) adsorbed on the Fe (001) surface (Fe^{II}), we

proposed an additional molecular simulation using a charged iron upper surface (Fe^{II}), which is seen in Fig. 7. For R1, R2, and R3, the corresponding E_{ads} are -51, -52, and -55 kJ/mol (refer to Table 5).

Table 5. Calculated quantum chemical parameters of the suggested inhibitors with charged metal surface, using Mm+ method

Component	Total energy, (kJ/mol)	E_{ads} , (kJ/mol)
R1	64.69	-51.12
R2	75.47	-52.53
R3	99.35	-55.10
$\text{Fe}^{\text{II}}\text{crystal}$	21133.46	
Complex(Fe^{II} -InhR1)	21147.03	
Complex(Fe^{II} -InhR2)	21156.40	
Complex(Fe^{II} -InhR3)	21177.71	

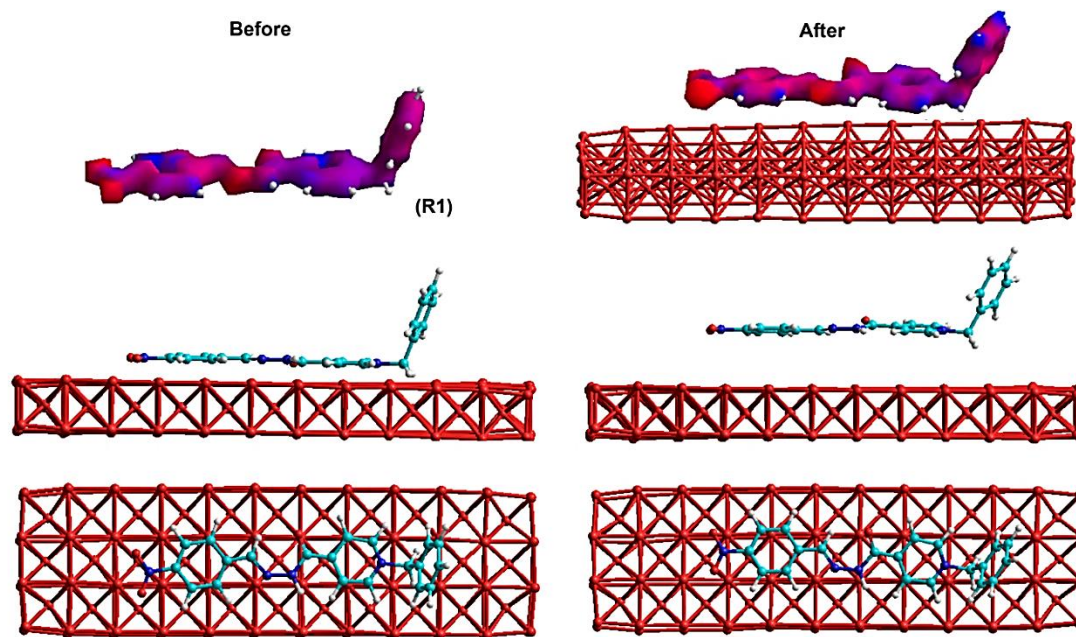


Figure 7. Side and top views of most stable adsorption conformations and electrostatic potential maps for inhibitor A1 on Fe (001) surface (Fe^{II}) (before and after simulation)

The E_{ads} data in Tables (3,4) make it evident that the inhibitor molecule's adsorption process on the charged iron upper surface was roughly equivalent to that of the inhibitor molecule on the uncharged iron upper surface. This explains why there is a strong adsorption process between the molecular system and the metal surface whether the upper surface is charged or uncharged.

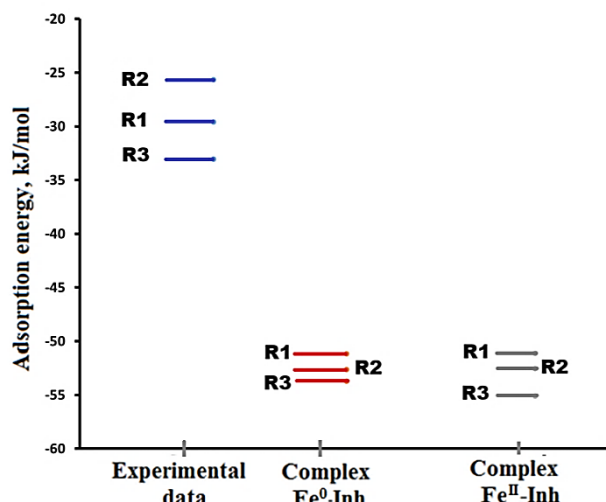


Figure 8. Diagram of adsorption energy for the complexes that form between the inhibitor molecule and the charged and uncharged iron surfaces

Additionally, the correlation between the theoretical E_{ads} calculations and the experimental evidence of $\Delta G^{\circ}_{\text{ads}}$ leads to the conclusion that inhibitor molecules with charged and uncharged

iron surfaces can work in concert to protect metal surfaces in two different scenarios (see Fig. 8).

3.5. The mechanism of corrosion inhibition

Lastly, the physicochemical properties of the Fe surface serve as the mechanism of corrosion inhibition for this work. We proposed that altering the metal surface's electrical environment could be utilized to illustrate adsorption in the point of view of the experimental findings and theoretical calculations. Fig. 9 illustrates how the pyridinium salts trying to adsorb on the iron surface by removing environmental corrosive fragments. Several reports have shown and proven that iron metal surface in acidic solutions are electron-deficient [58-62].

The ability of particular function groups to attach to the inhibitor molecules on the metal surface explains why the inhibitor can be adsorbed on the metal surface. When the concentration of the inhibitor is raised, the formation of a protective layer of inhibitor molecules on the metal/solution interface increases the effectiveness of inhibition. A thin layer of organic inhibitor molecules forms in the solution as a result of the alteration in the electrical environment for Fe surfaces, which promotes organic inhibitor molecule adsorption. These organic salt compounds can mix in solution because the N and S electrons are not shared. Because of electrostatic interactions, organic molecules may have a physisorbed effect on metal surfaces [63-65].

An envisioned process involving the interaction of the metal/acid mixture could absorb the organic molecule. Fig. 9 illustrates the following procedures: (i) Physisorption, which is the electrostatic attraction of protonated organic molecules that inhibit currently adsorbed ions; (ii)

chemisorption, which is the interaction of charged particles and unpaired electrons of heteroatoms with the unoccupied d-orbital of iron surface atoms; and (iii) the relationship between the unoccupied orbital of the molecule that inhibits (retro-donation) and the d-electron of the iron surface atom.

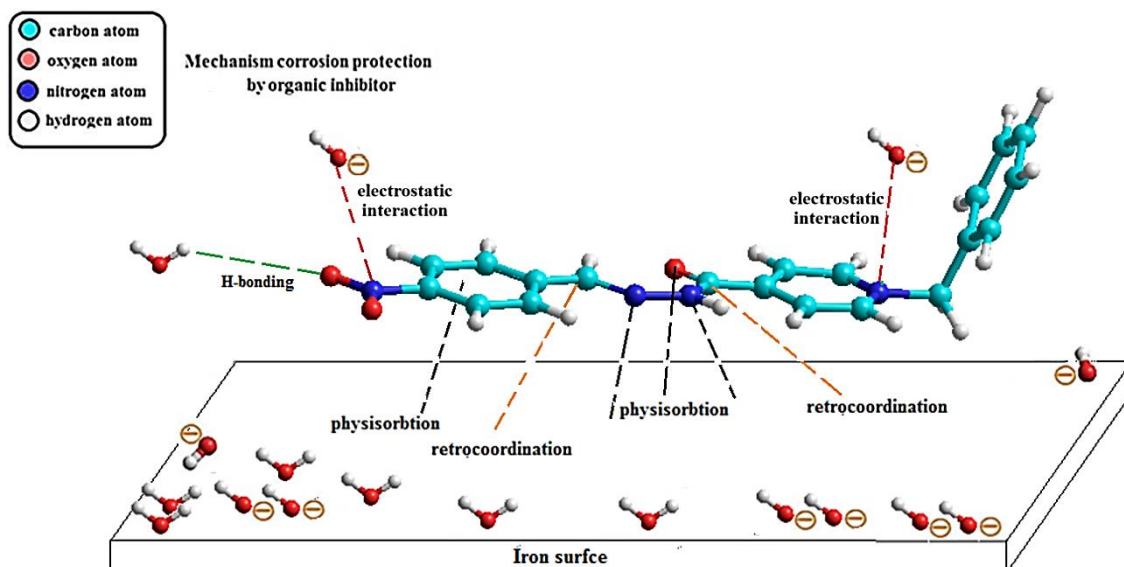


Figure 9: The mechanism by which inhibitor molecules interact with the surface environment of mild steel has been suggested

4. CONCLUSION

Pyridinium salts (R1-R3) were successfully used as organic corrosion inhibitors on the iron metal surface in 1M H_2SO_4 solution at room temperature. The inhibition efficiency (IE%) data showed that the prepared compounds exhibited high efficiency in reducing and preventing corrosion electrochemical process on the iron metal surface. The free energy adsorption values (R1, R2 & R3), which offered useful information to elucidate the nature of the organic molecules' interactions with the metal, were being influenced by the physical process of adsorption. The results of the three inhibitors under investigation were compared with theoretical data obtained from quantum molecular orbital simulations. The mechanism of the interaction between the iron surface and the organic corrosion inhibitor was made to be more clear by theoretical approaches.

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Conflicts of interest

There are no conflicts to declare

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IZVOD

PIRIDINIJUMOVE SOLI KAO INHIBITORI KOROZIJE ZA MEKI ČELIK U KISELOM RASTVORU: TEORIJSKI I EKSPERIMENTALNI PRISTUPI

Nove piridinijumske soli, i to: 1-benzil-4-(2-(4-nitrobenziliden)hidrazinil)piridin-1-ijum-bromid (R1), 1-butil-4-(2-(4-nitrobenziliden)hidrazinil)piridin-1-ijum-bromid (R2) i 4-(2-(4-nitrobenziliden)hidrazinil)-1-(2-okso-2-feniletil)piridin-1-ijum-bromid (R3), uspešno su sintetisane kao organski inhibitori korozije za niskougljeni čelik. Evaluacija ovih soli u 1 M H₂SO₄ izvršena je primenom metode gubitka mase, pri čemu je eksperiment trajao 24 sata na sobnoj temperaturi. Prilikom ispitivanja različitih koncentracija, utvrđena je visoka efikasnost inhibicije za sve navedene soli (R1–R3). Brzina korozije se smanjivala sa porastom koncentracije inhibitora, dok su se stepen pokrivenosti površine i efikasnost inhibicije povećavali. Na osnovu izračunatih podataka dobijenih analizom adsorpcije, predviđeno je da se proces vezivanja ovih jedinjenja (R1, R2 i R3) za površinu odvija putem fizisorpcije.

Za ove organske soli-inhibitore sprovedena su ispitivanja na nivou poluempirijskih molekulskih orbitala i primenjen je pristup molekulske mehanike kako bi se utvrdila korelacija između eksperimentalnih i teorijskih podataka. Pored toga, priroda interakcije između molekula organskog inhibitora i metalne površine gvožđa određena je putem teorijskih simulacija.

KLjučne reči: piridinijumske soli, fizisorpcija, molekulska simulacija, inhibitori korozije.

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