Synthesis New Pyridinium Salts as Corrosion Inhibitors for Mild Steel in 1 M H₂SO₄

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Abstract

Some new pyridinium salts, namely 4-(4-Chloro-benzylidene-hydrazinocarbonyl)-1-phenyl-pyridinium bromide, C1: 4-(4-Chloro-benzylidene-hydrazinocarbonyl)-1-butyl-pyridinium bromide, C2: 4-(4-Chloro-benzylidene-hydrazinocarbonyl)-1-phenyl-pyridinium bromide, C3: were synthesized and Corrosion inhibitors for mild steel were tested in 1 M H₂SO₄ aqueous solution at 20 °C for 24 hours using weight loss measurements. The findings revealed that the inhibition efficiency of all pyridinium bromide derivatives converges at the maximum concentration. An increase in inhibitor concentration is associated with a decrease in corrosion rate, an increase in inhibition efficiencies, and an increase in surface degree of coverage. The physisorption effects for (C1, C2, and C3) were revealed by the free energy values of adsorption, which provided useful information for predicting the interaction between the metal surface and organic molecules as corrosion inhibitors.

Keywords:
Pyridinium salts
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1. Introduction

Corrosion inhibitors are commonly used to prevent metal dissolution, particularly in aqueous solutions [1]. Hydrochloric and sulfuric acids are widely used in the metallurgical industry in a variety of techniques such as pickling metals to extract scale, deactivation of gear in atomic power plants, chemical or electrochemical methods in oil refineries, and rocket fuel influences [2,3]. Factors in rocket science, etc. In general, corrosion inhibitors are applied in a limited amount to corrosive media with the aim of slowing the rate of corrosion by adsorption [4,5]. Organic compounds with heteroatoms, such as sulfur, nitrogen, oxygen, and a couple of bonds, use an adsorption mechanism to effectively prevent corrosion even at low concentrations [6,7]. Metal corrosion remains a global science issue because it affects the metallurgical, chemical, and oil industries. The increasing interest in the production of acid media has necessitated the gathering of data on mild steel's corrosion resistance to acid media attack [8]. Pickling, washing, and decaling are all businesses that use acids. They are violent because of their nature metal dissolution is slowed down by the use of inhibitors. Nitrogen, sulfur, and oxygen-containing compounds have been identified as potent inhibitors [9-11]. The metal ion acts as an electrophile and organic compound with N, O, S and P atoms that have nucleophilic centers and are easily shared.

Several organic derivatives have also been studied in acidic media as corrosion inhibitors for various metals and alloys [12-16]. We generated some pyridinium bromide salts using Schiff base compounds and N-alkylation reaction with alkyl halides in this study. In 1M H₂SO₄ solutions, mild steel corrosion and corrosion inhibition without and with weight loss measurements were performed on prepared pyridinium salts for 24 hours at 20 °C.

2. Experimental

2.1 Materials

Both chemicals (reagents and solvents) were used exactly as they were obtained.

2.2 Instrumentation

The prepared compounds' infrared spectra were recorded using a SHIMADZU Company FTIR 8300 Fourier transform infrared spectrophotometer as potassium bromide (KBr) discs in the wave number range of (4000-400) cm⁻¹ and ¹H-NMR (DMSO-d6). The open capillary method was used to calculate melting points using a hot stage Gallenkamp melting point apparatus, and the results were uncorrected. To assess the composition of mild steel samples, Spectromax (2009, Germany) was used (State Company for Inspection and Rehabilitation, Ministry of Industry and Materials, Baghdad).

Synthesis of pyridinium bromide salts

Pyridinium bromide derivatives inhibitors, such as: namely 4-(4-Chlorobenzylidene-hydrazinocarbonyl)-1-phenyl-pyridinium bromide, C1: 4-(4-Chlorobenzylidene-hydrazinocarbonyl)-1-butyl-pyridinium bromide, C2:
Chlorobenzylidene-hydrazinocarbonyl)-1-phenyl-pyridinium bromide, C3; were synthesized as follow:

- Preparation compound of Schiff base [17]. The Schiff base compound was made by refluxing equimolar amounts (0.01 mol) of isonicotinic acid hydrazide and p-chlorobenzaldehyde in 25 mL ethanol for 8 hours with a few drops of glacial acetic acid. After cooling, the Schiff base compound was precipitated, filtered, and distilled by recrystallization from ethanol.

- Preparation of pyridinium bromide derivatives (C1-C3) [18]. The pyridinium bromide derivatives were prepared by reaction a mixture of (0.01 mol) of the prepared Schiff base compound and (0.01 mol) of (benzyl bromide, butyl bromide and phenacyl bromide). In a round-bottomed flask fitted with a reflux condenser, in (2 mL) absolute ethanol was allowed to stand overnight at room temperature. The mixture was then heated for 25 hours at reflux temperature. After evaporating the solvent, the resulting solid was washed with three portions of (10 mL) diethyl ether after the resulting solution was evaporated. Figure 1 depicts the molecular formulas of potential inhibitors.

![Figure 1. The molecular formula of suggested inhibitors (C1, C2 and C3).](image)

### 2.3 Preparation solutions

Dilution of analytical grade (98 %) H₂SO₄ with distilled water yielded an aggressive solution of 1M H₂SO₄. The inhibitor concentrations ranging from (1×10⁻² to 5×10⁻⁴ M) were prepared in 1M H₂SO₄ solution.

### 2.4 Weight loss measurements

The remaining iron was in a sheet of mild steel with the following composition percentages (0.002 % P, 0.288 % Mn, 0.03 % C, 0.0154 % S, 0.0199 % Cr, 0.002 % Mo, 0.065 % Cu, and 0.0005 % V). The mild steel sheet was mechanically cut into a disk form with a diameter of 12 inches (2.5 cm). To achieve a smooth surface, these disc shapes were polished with 2000 grade emery paper. Then they used distilled water, alcohol, and acetone to disinfect. Before being used in corrosion tests, the treated specimens were placed in a moisture-free desiccator. Initially, mild steel specimens were weighed in an electronic balance. The specimens were then suspended and completely submerged in a 250 ml beaker containing 1M sulfuric acid in the presence and absence of inhibitors after 24 hours exposure time at 20 °C, the specimens were removed, washed with water to eliminate any corrosion products, and then washed with acetone. They were then reweighted after being dried in a desiccator. The mass loss measurements were carried out according to the ASTM system [19,20]. The experiments were carried out twice to ensure that the findings were accurate and the weight loss's average value is stated Weight loss made it possible to calculate the average corrosion rate in (mg cm⁻² h⁻¹). The corrosion rate of mild steel was calculated using the following formula (1) [21]:

\[ W = \frac{\Delta m}{S \times t} \]  

where \( m \) is the mass loss (in grams), \( S \) is the area (in square meters), and \( t \) is the immersion time (hours). The percentage inhibition efficiency (E %) was determined using the following equation (2) [22]:

\[ E\% = \frac{W_{corr} - W_{corr(inh)}}{W_{corr}} \times 100 \]

where \( W_{corr} \) and \( W_{corr(inh)} \) are the mild steel corrosion rates in the presence and absence of an inhibitor, respectively.

### 3. Results and Discussion

Scheme 1 shows the current work's preparation of pyridinium bromide derivatives (C1-C3).

![Scheme 1. Synthesis steps of the pyridinium salts (C1, C2, and C3).](image)

The preparation of pyridinium bromide derivatives (C1, C2, and C3) were achieved by using isonicotinic acid hydrazide to obtain Schiff's base reaction with p-chlorobenzaldehyde was one of the reactions mentioned above. The reaction is then accompanied by an alkyl bromide substitution reaction.

Table 1 summarizes the FT-IR spectral data and physical properties of prepared compounds, as well as, the ¹H-NMR. Table 2 lists the spectral data of compounds (C1-C3) in ppm.
Table 1. FTIR spectral data and physical properties of prepared compounds.

| Compound | Chemical formula | M.W. (g/mol) | Color | M.P.°C | Yield % | FTIR data, ν, cm⁻¹ |
|----------|------------------|--------------|-------|--------|---------|--------------------|
| 1        | Isonicotinic hydrazide | C₆H₇N₃O | White | 173    | –       | Aminic (N–H) 3300 and 3173 3049 aliphatic (C–H) 2860 amide (C=O) 1668 aromatic (C–H) 3049 aliphatic (C–H) 2860 |
| 2        | P-Chloro benzaldehyde | C₇H₅ClO | White | 48     | –       | Aliphatic (C–H) 2856 Aromatic (C–H) 3086 1687 Aldehyde (C=O) |
| A        | Isonicotinic acid (4-chloro-benzylidene)-hydrazide | C₁₄H₁₄ClN₃O | White | 195 79 |         | 3029 Aliphatic (C–H) 2943 Azomethine (C=N) 1631 Aromatic (C–H) 3029 Aliphatic (C–H) 2943 |
| C1       | 3-(4-Chlorobenzylidene-hydrazinocarbonyl)-1-phenyl-pyridinium bromide | C₁₉H₁₃BrClN₃O | Brown Gummy | 75    |         | amide (C=O) 1677, amide (N–H) 3111, imine (N=C) 1637, aromatic (C–H) 3034, aliphatic (C–H) 2975, amide (C=O) 1677, amide (N–H) 3111, imine (N=C) 1637 |
| C2       | 3-(4-Chlorobenzylidene-hydrazinocarbonyl)-1-butyl-pyridinium bromide | C₁₉H₁₃Br₂N₃O | Brown Gummy | 73    |         | amide (C=O) 1656, amide (N–H) 3397, imine (N=C) 1615, aromatic (C–H) 3100, aliphatic (C–H) 2971 |
| C3       | 3-(4-Chlorobenzylidene-hydrazinocarbonyl)-1-phenacyl-pyridinium bromide | C₂₀H₁₇BrN₃O₃ | Yellow Gummy | 82    |         | aromatic (C–H) 3092, aliphatic (C–H) 2834, amide (C=O) 1675, amide (N=H) 3178, imine (N=C) 1675 |

Table 2. The ¹H-NMR spectral data of compounds (C1–C3) in ppm.

| Comp. No. | Compound structure | ¹H-NMR data of (δ-H) in ppm |
|-----------|-------------------|------------------------------|
| C1        | ![C1 Compound Structure](image) | 1H of N–H (–CO–NH– moiety) (11.6); 4H of pyridine-ring (8.7-9.4); 1H of N=CH– (8.5); 9H of phenyl-rings (7.1-8.2); 2H of –N’–CH₂ group (6.0); 1H of O–H (3.4, tautomerism of –CO–NH– moiety) |
| C2        | ![C2 Compound Structure](image) | 1H of N–H (–CO–NH– moiety) (12.6); 4H of pyridine-ring (8.8-9.3); 1H of N=CH– (8.5); 4H of phenyl-rings (7.4-8.3), 2H of –N’–CH₂ group (4.6); 7H of aliphatic chain (0.9-2.0) |
| C3        | ![C3 Compound Structure](image) | 1H of N–H (–CO–NH– moiety) (12.6); 4H of pyridine-ring (8.6-9.2); 1H of –N=CH– (8.5); 9H of phenyl-rings (7.4-8.2), 2H of –N’–CH₂ group (6.5); |
After 24 hours of immersion at 20 °C, the results of corrosion rate and inhibition efficiency obtained from weight loss measurements with different concentrations of suggested inhibitors (C1, C2, C3) are summarized in Table 3 and depicted in Figures 2 and 3.

Table 3. Shows the corrosion rate (Wcorr.), inhibition efficiency (E%), surface coverage (θ) and normal free energy of adsorption (ΔG°ads) for mild corrosion Steel was tested in 1M H₂SO₄ using weight loss measurements over a 24-hour period at 20 °C.

| Concentration (M) | Corrosion rate (mg.cm⁻².h⁻¹) | E%   | θ    | ΔG°ads (kJ. mol⁻¹) |
|-------------------|------------------------------|------|------|-------------------|
| Blank             | 0.344                        |      |      |                   |
| C1                | 0.1956                       | 42.87| 0.4287|                   |
| 1×10⁻³            | 0.0891                       | 74.09| 0.7409|                   |
| 1×10⁻²            | 0.0692                       | 79.88| 0.7979|                   |
| 5×10⁻³            | 0.0110                       | 96.79| 0.9679|                   |
| C2                | 0.2178                       | 36.68| 0.3668|                   |
| 1×10⁻³            | 0.1201                       | 65.08| 0.6508|                   |
| 5×10⁻³            | 0.0350                       | 90.26| 0.9026|                   |
| 1×10⁻²            | 0.0292                       | 91.51| 0.9151|                   |
| C3                | 0.0597                       | 82.64| 0.8264|                   |
| 1×10⁻³            | 0.0219                       | 93.63| 0.9363|                   |
| 5×10⁻³            | 0.0088                       | 97.44| 0.9744|                   |
| 1×10⁻²            | 0.0023                       | 99.33| 0.9933|                   |

Figure 2. For suggested inhibitors, the effect of inhibitor concentrations on the rate of corrosion for mild steel in 1M H₂SO₄ at 20 °C (C1, C2, and C3).

Figure 3. Effect of inhibitor concentrations on mild steel 1M H₂SO₄ inhibition efficiency at 20 °C for suggested inhibitors (C1, C2, C3).
Table 3 shows that as the inhibitor concentration is increased, the defense efficiency improves, with the highest inhibition efficiencies reached at 10\(^{-2}\) M. As a result of the comparison, the inhibition efficiency of (C1, C2, and C3) is roughly comparable. The effect of organic molecular structure on inhibition efficiency may explain the rapprochement in inhibition efficiency.

Efficient damping inhibitors, as well as the adsorption process. Basic information of adsorption isoforms can be provided to explain the interaction between organic compounds and mineral surfaces. Therefore, the degree of surface coverage values (θ) for different inhibitor concentrations was achieved in 1M H\(_2\)SO\(_4\) from weight loss measurements (θ = E (%) / 100) (listed in Table 3) at 20 °C and tested using the Langmuir isothermal relationship (3) [23]:

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + C
\]

where C is the concentration in M, cades is the equilibrium constant of the adsorption process. According to the Langmuir isotherm, the Kads values can be calculated from the straight line intersections of C / plot versus C (Figure 3). The Kads are related to the standard free absorption energy, Goads, by the following equation (the value 55.5 is the molar concentration of water in solution in M):

\[
K_{ads} = \frac{1}{55.5} \exp \left( - \frac{\Delta G_{ads}}{RT} \right) \quad \ldots(4)
\]

Table 3 shows that the values of the standard free energy of absorption are negative to indicate that the adsorption processes of all proposed inhibitors (C1, C2, and C3) were spontaneous processes on the surface of mild steel after 24 hours of immersion at 30 °C and this is to give meaning to the observed interaction between Suggested damper and metal surface. Here, the adsorbent molecule moves near the surface of the metal causing the electrons to begin to interfere with the surface atoms causing the decomposition of the proposed inhibitors [24-27]. It is generally accepted that the adsorption of an organic inhibitor on a metallic surface in an acidic medium usually includes the formation of a metal inhibitor compound by combining the inhibitor with the newly generated Fe\(^{2+}\) ions on the surface of the steel [28]:

\[
\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \quad \ldots(5)
\]

\[
\text{Fe}^{2+} + \text{Inh(ads)} \rightarrow [\text{Fe-Inh}]^{2+}(\text{ads}) \quad \text{(Metal-inhibitor complex)} \quad \ldots(6)
\]

As a result, the mineral inhibitor complex will serve as a protective layer for anodic sites, preventing Fe\(^{2+}\) sites from forming. As a result, it’s possible that a compact metal inhibitor complex forming is lower at lower concentrations of the proposed inhibitors. The adsorption mechanism of particular inhibitors is determined by the action of organic molecular adsorption molecules with N or O atom. More than one functional group has been documented to cause changes in the electron density of the molecule, which can influence absorption activity [29]. The proposed inhibitors can absorb with the corroded metal surface through the compacted metal retarder complex located at the anodic sites, reducing the loss of (Fe) atoms from the surface via electrochemical dissolution.

The values of \(\Delta G_{ads}\) as listed in Table 3 revealed physical adsorption [29]. The proposed inhibitor (C3) showed value \(\Delta G_{ads} = 32.50\ \text{kJ/mol}\), which was verified by E% values (82-99) for various concentrations, as shown in Table (3). Despite the low concentration of (C3) (0.0005M), E% is higher than E% values for (C1) and (C2). Because of molecular formula of C3 that made the electron density around the group \(-\text{N}=\text{CH}\−\) is higher. The interaction between the organic molecule (C3) and the metal surface is improved by the uniform distribution of electron density on the surface of the organic molecule (C3), as well as, for C1 and C2.

Finally, Figure 5 depicts the reaction mechanism, which shows the modeling representation of the nitrogen and oxygen atoms adsorption process, as well as, the aromatic groups of the proposed inhibitor molecules on the mild surface.
4. Conclusion
Pyridinium compounds (C1, C2, and C3) have been successfully used as corrosion inhibitors on the surface of mild steel in a 1M H₂SO₄ aqueous solution at 20 °C. The results of inhibitory efficacy (E%) showed interesting inhibitory effects of the proposed inhibitors. The values of the free energy of adsorption showed the effect of physical adsorption (C1, C2, C3) and gave useful information to explain the interaction between the metal surface and the organic molecules.

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