Electrochemical and Gravimetric Corrosion Inhibition Investigations of A Heterocyclic Schiff Base Derived From 3-Formylinodole.

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Abstract: The corrosion inhibition efficiency of Schiff base, 3-formylinodole-3-aminobenzoic acid (3FI3ABA) on mild steel (MS) in 1.0 M HCl solution have been investigated using weight loss measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies. 3FI3ABA exhibited good inhibition on mild steel in HCl medium even at low concentrations and the inhibition efficiencies increases with increase in concentration of the inhibitor. The adsorption of inhibitor on the surfaces of the corroding metal obeys Langmiur isotherm. Polarization studies revealed that 3FI3ABA act as a mixed type inhibitor. Thermodynamic parameters (K_{ads}, ΔG_{ads}) were calculated using Langmiur adsorption isotherm.

Keywords: Corrosion inhibitors, Impedance, Isotherm, Mild Steel, Schiff base.

I. Introduction

Schiff bases, are organic molecules possessing azomethine linkage (C=N), have innumerable advantages, right from pharmaceutical applications to the corrosion inhibitions, in the various fields of science. The hetero atoms present in these molecules are of key importance and are responsible for the corrosion inhibition in acidic media on the metal surface [1-3]. Some recently reported Schiff bases showed effective inhibition for mild steel (MS), Aluminum, Copper and Zinc in acidic media [4-11]. Enormous use of hydrochloric acid for acid pickling, de-scaling and cleaning process of mild steel surface are the major reasons for the corrosion problems in the world. Increasing efforts have been made to study the corrosion behavior of metals and mechanism of inhibition during the past decade mainly through electrochemical investigations [8,9]. Limited work has been reported for the corrosion inhibition of compounds derived from 3-formylinodole in acid media. The present investigation was undertaken to examine the corrosion inhibition capacity and mechanism of inhibition of a novel heterocyclic Schiff base (3FI3ABA) molecules derived from 3-formylinodole and 3-aminobenzoic acid in 1M HCl solution on MS. The study was performed using weight loss measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization analysis.

II. Experimental

Inhibitor

Heterocyclic Schiff base was obtained by the condensation of equimolar mixture of 3-formylinodole and 3-amino benzoic acid in ethanol. The reaction mixture was refluxed for 2 hours, evaporated and cooled in ice bath to obtain yellow coloured compound. Figure 1 shows the molecular structure of heterocyclic Schiff base 3FI3ABA. Anal.caled for C_{16}H_{12}N_{2}O_{2}: C, 72.72; H, 4.55; N, 10.61 ; O, 12.12%. Found. C, 70.96; H, 5.10; N, 9.98 ; O, 12.17% ; m.p. = 180 ^\circ C; 1R (KBr): ν C=O = 1600 cm^{-1}. ^1Hnmr: δ_{COOH} 11.99, δ_{CH=N} 9.79, δ_{NH} 6.83. ^13Cnmr: δ_{COOH} 187.56, δ_{CH=N} 130.32. Mass:M^+ peak m/z:264 (Base peak).

Figure 1: Molecular Structure of 3FI3ABA

Solutions

The aggressive solutions of 1M HCl were prepared by dilution of A.R grade 37% of HCl (Merck) with de-ionized water. Inhibitor solutions were prepared in the range, 0.1mM-1mM concentrations.

Weight loss measurements

Mild steel specimens of dimension 1.5x 2x 0.1 cm were cut abraded with various grades of silicon carbide papers (200, 400, 600, 800, 1000, 1200 and 2000). The exact area and thickness of each coupon were measured and washed with distilled water containing detergent. Specimens were then degreased again with acetone and finally dried. After weighing with sensitive electronic balance, specimens were immersed in 50ml
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acid solutions (non-de aerated) at 28°C in the absence and presence of the inhibitor, 3FI3ABA, using hooks and fishing lines. Weight loss of metal specimens was noted at every 24 h time interval for five days. The experiments were carried out in duplicate and the average values were reported. The corrosion rate (v) is calculated by the following equation [8].

\[ v = \frac{W}{St} \]  
where W is the average weight loss of coupon, S is the total area of specimen and t is the time of treatment.

The percentage of inhibition efficiency (\( \eta \)) is defined by [12].

\[ \eta_\% = \frac{\nu_0 - \nu}{\nu_0} \times 100 \]  

where \( \nu_0 \) and \( \nu \) are the corrosion rates of uninhibited and inhibited specimens respectively.

Electrochemical Impedance Spectroscopy (EIS)

The EIS measurements were performed in a three electrode assembly. Saturated calomel electrode (SCE) was used as the reference electrode. Platinum electrode having 1cm² area was taken as counter electrode. Metal specimens with an exposed area of 1cm² were used as the working electrode. The EIS experiments were carried out on a Ivium compactstat-e electrochemical system. 1M HCl acid (no deaeration, no stirring) was taken as the electrolyte and the working area of the metal specimens were exposed to the electrolyte for 1 h prior to the measurement. EIS measurements were performed at constant potential (OCP) in the frequency range from 1 KHz to 100 mHz with amplitude of 10 mV as excitation signal. The percentage of inhibitions from impedance measurements were calculated using charge transfer resistance values by the following expression [2]:

\[ \eta_{EIS} \% = \frac{R_{ct}-R'_{ct}}{R_{ct}} \times 100 \]  
where \( R_{ct} \) and \( R'_{ct} \) are the charge transfer resistances of working electrode with and without inhibitor respectively.

Potentiodynamic polarization

Electrochemical polarization studies of MS specimens in 1M HCl with and without inhibitor were performed by recording anodic and cathodic potentiodynamic polarization curves. Polarization plots were obtained in the electrode potential range from -100 to +100 mV Vs corrosion potential (E_corr) at a scan rate of 1mV/sec. Tafel polarization analysis were done by extrapolating anodic and cathodic curves to the potential axis to obtain corrosion current densities (I_corr). The percentage of inhibition efficiency (\( \eta_{pot\%} \)) was evaluated from the measured I_corr values using the following relation [13]:

\[ \eta_{pot\%} = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \]  
where \( I_{corr} \) and \( I'_{corr} \) are the corrosion current densities of the exposed area of the working electrode in the absence and presence of inhibitor.

From the slope analysis of the linear polarization curves in the vicinity of corrosion potential of blank and different concentrations of the inhibitor, the values of polarization resistance (\( R_p \)) in 1M HCl solution were obtained. From the evaluated polarization resistance, the inhibition efficiency was calculated using the relationship

\[ \eta_{pol\%} = \frac{R'_{p}-R_p}{R_p} \times 100 \]  
where \( R'_{p} \) and \( R_p \) are the polarization resistance in the presence and absence of inhibitor respectively [2].

III. Results And Discussion

Weight loss measurements

The corrosion rates and inhibition efficiencies obtained for MS specimens for a period of 24 h are listed in Table 1. For MS specimens the corrosion rate markedly decreased with inhibitor concentration. This response is due to the fact that the surface coverage of the inhibitor molecules on the metal through adsorption increases with increase in concentration [14]. A maximum inhibition efficiency of 95% was obtained for 0.8mM. Fig. 2 shows the variation inhibition efficiency with immersion time for the inhibitor concentrations 0.1, 0.4 and 0.8mM. For 0.1 and 0.4mM concentrations the inhibition efficiencies rose up to 72 hr and will not changed further considerably. For 0.8mM concentration, the percentage of inhibition efficiency almost remained as constant for the studied period.
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Table 1: The corrosion rate and percentage of inhibition efficiency obtained for MS specimens immersed in 1M HCl at 28 °C for 24 h in the presence and absence of 3FI3ABA

<table>
<thead>
<tr>
<th>C (mM)</th>
<th>Corrosion rate (mmy⁻¹)</th>
<th>Inhibition efficiency (η_W %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.23</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>1.12</td>
<td>73.5</td>
</tr>
<tr>
<td>0.2</td>
<td>1.02</td>
<td>75.8</td>
</tr>
<tr>
<td>0.3</td>
<td>0.80</td>
<td>81.1</td>
</tr>
<tr>
<td>0.4</td>
<td>0.76</td>
<td>82.2</td>
</tr>
<tr>
<td>0.5</td>
<td>0.52</td>
<td>87.8</td>
</tr>
<tr>
<td>0.6</td>
<td>0.45</td>
<td>89.4</td>
</tr>
<tr>
<td>0.7</td>
<td>0.37</td>
<td>91.3</td>
</tr>
<tr>
<td>0.8</td>
<td>0.21</td>
<td>95.0</td>
</tr>
</tbody>
</table>

![Figure 2: Variation of inhibition efficiency with immersion time](image)

Comparison of inhibition efficiency of Schiff base with its parent amine

To compare the inhibition efficiencies of Schiff base and parent amine, weight loss measurements of MS specimens were performed in 1M HCl at 28 °C. The percentage of corrosion inhibition efficiencies obtained for Schiff base and parent amine on MS specimens is listed in Table 2. For MS specimens the inhibition efficiency of the Schiff base 3FI3ABA was markedly higher than that of 3-aminobenzoic acid for the studied concentrations. This investigation clearly establishes the role of azomethine linkage (C=N) present in the Schiff base which actively participate in the corrosion inhibition mechanism.

Table 2: Comparison of inhibition efficiency of Schiff base and parent amine

<table>
<thead>
<tr>
<th>C (mM)</th>
<th>MS specimens (η_W %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parent Amine</td>
</tr>
<tr>
<td>0.1</td>
<td>48.9</td>
</tr>
<tr>
<td>0.4</td>
<td>55.1</td>
</tr>
<tr>
<td>0.7</td>
<td>67.1</td>
</tr>
</tbody>
</table>

Adsorption isotherm and free energy of adsorption

The mechanism of adsorption and the surface behavior of organic molecules can be easily viewed through adsorption isotherms. Different models of adsorption isotherms considered are Langmiur, Temkin, Frumkin and Freundlich isotherms. For the evaluation of thermodynamic parameters it is necessary to determine the best fit isotherm with the aid of correlation coefficient (R²). Among the isotherms mentioned above, the best description of the adsorption behavior of 3FI3ABA on MS specimens in 1M HCl was Langmiur adsorption isotherm which can be expressed as

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

where C is the concentration of the inhibitor, \( \theta \) is the fractional surface coverage and \( K_{ads} \) is the adsorption equilibrium constant [15]. Fig. 3 represents the adsorption plots of 3FI3ABA obtained by the weight loss measurements of MS steel specimens in 1M HCl at 28 °C.
The adsorption equilibrium constant $K_{ads}$ is related to the standard free energy of adsorption $\Delta G^0_{ads}$, by

$$\Delta G^0_{ads} = -RT \ln (55.5 K_{ads})$$

Where 55.5 is the molar concentration of water, $R$ is the universal gas constant and $T$ is the temperature in Kelvin [16]. From the adsorption isotherm, $K_{ads} = 16666$. $\Delta G^0_{ads}$ for 3FI3ABA on MS showed negative values indicating the spontaneity of the process. The value of $\Delta G^0_{ads}$ up to $-20kJ/mol$ is an indication of the electrostatic interaction of the charged molecule and the charged surface of the metal (physisorption) while $\Delta G^0_{ads}$ is more negative than $-40kJ$ implies that inhibitor molecules are adsorbed strongly on the metal surface through co-ordinate type bond (chemisorption) [16-18]. In the present investigation, 3FI3ABA molecules showed $\Delta G^0_{ads} = -34.4kJ$ suggesting that the adsorption of inhibitor involves both electrostatic-adsorption and chemisorptions on MS.

EIS measurements

The corrosion response of MS in 1M HCl in the presence and absence of inhibitor has been investigated using Electrochemical Impedance Spectroscopy at 28°C. Fig. 4 represents the Nyquist plots of MS specimens in 1M HCl. It is evident from the plots that the impedance response of metal specimens showed a marked difference in the presence and absence of the inhibitor 3FI3ABA. The semicircles showed slight irregularity which may be attributed to the roughness or non homogeneous nature of the metal surface [19-22]. The capacitance loop intersects the real axis at higher and lower frequencies. At high frequency end the intercept corresponds to the solution resistance ($R_s$) and at lower frequency end corresponds to the sum of $R_s$ and charge transfer resistance ($R_{ct}$). The difference between the two values gives $R_{ct}$. The value of $R_{ct}$ is a measure of electron transfer across the exposed area of the metal surface and it is inversely proportional to rate of corrosion [23].

$$Z_{CPE} = \frac{1}{Y_0 (j\omega)^n}$$

(8) Where $Y_0$ is the magnitude of CPE, $n$ is the exponent (phase shift), $\omega$ is the angular frequency and $j$ is the imaginary unit. CPE may be resistance, capacitance and inductance depending upon the values of $n$ [5]. In all experiments the observed value
of n ranges between 0.8 and 1.0, suggesting the capacitive response of CPE. The EIS parameters such as R<sub>ct</sub>, R<sub>s</sub> and CPE and the calculated values of percentage of inhibition (η<sub>EIS%</sub>) are listed in Table 3.

**Table 3: Electrochemical Impedance parameters of MS specimens, in 1M HCl at 28°C in the absence and presence of 3FI3ABA**

<table>
<thead>
<tr>
<th>C (mM)</th>
<th>R&lt;sub&gt;ct&lt;/sub&gt; (Ωcm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>CPE (μF cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>R&lt;sub&gt;s&lt;/sub&gt; (Ωcm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>η&lt;sub&gt;EIS%&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.0</td>
<td>97.06</td>
<td>5.42</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>47.9</td>
<td>78.72</td>
<td>5.84</td>
<td>31.1</td>
</tr>
<tr>
<td>0.5</td>
<td>151.0</td>
<td>91.31</td>
<td>13.06</td>
<td>78.1</td>
</tr>
<tr>
<td>0.7</td>
<td>288.0</td>
<td>62.09</td>
<td>17.59</td>
<td>88.5</td>
</tr>
<tr>
<td>0.8</td>
<td>348.0</td>
<td>53.73</td>
<td>20.04</td>
<td>90.5</td>
</tr>
</tbody>
</table>

From Table 3 it is clear that R<sub>ct</sub> values are increased with increasing inhibitor concentration. Decrease in capacitance values CPE with inhibitor concentration can be attributed to the decrease in local dielectric constant and/or increase in the thickness of the electrical double layer. This emphasis the action of inhibitor molecules by adsorption at the metal–solution interface [28]. The percentage of inhibitions (η<sub>EIS%</sub>) showed a regular increase with inhibitor concentration. A maximum of 90.5% inhibition efficiency could be achieved at an inhibitor concentration of 0.8 mM.

**Potentiodynamic polarization studies**

Potentiodynamic polarization curves for 3FI3ABA in 1M HCl on MS specimens are shown in Fig.6. Polarization parameters like corrosion current densities (I<sub>corr</sub>), corrosion potential (E<sub>corr</sub>), cathodic Tafel slope (b<sub>c</sub>), anodic Tafel slope (b<sub>a</sub>), and inhibition efficiency (E<sub>p</sub>) are listed in Table 4. A prominent decrease in the corrosion current density (I<sub>corr</sub>) was observed in the presence of inhibitor 3FI3ABA. A lowest value of I<sub>corr</sub> was noticed for the inhibitor solution of concentration 0.8mM which exhibited a maximum inhibition efficiency of 90%. Since the value of b<sub>a</sub> changes appreciably in the presence of 3FI3ABA, it may be assumed that the inhibitor molecules are more adsorbed on anodic sites. Generally if the shift of E<sub>corr</sub> is >85 with respect to E<sub>corr</sub> of uninhibited solution, the inhibitor can be viewed as cathodic or anodic type [18,29,30]. In the present study the maximum shift of E<sub>corr</sub> is 25mV, suggesting that 3FI3ABA acts as a mixed type inhibitor for MS specimens in 1M HCl. Similar results were reported by Sam John et al [9].

![Figure 6: Tafel plots of MS specimens in 1M HCl at 28°C, with and without inhibitor](image)

**IV. Mechanism of Inhibition**

It is well known that the surface of the metal is positively charged in acidic media [31]. It is believed that the Cl<sup>-</sup> ions could be specifically adsorbed on the metal surface and creates an excess of negative charge on the surface. This will favour the adsorption of protonated Schiff base (3FI3ABAH<sup>+</sup>) on the surface and hence reduce the dissolution of Fe [32]. Besides this electrostatic interaction between the protonated Schiff base and the metal surface other possible interactions are i) interaction of unshared electron pairs in the molecule with the metal ii) Interaction of π-electrons with the metal and iii) a combination of types (i–ii) [33-34]. If one examines the structure of Schiff base (3FI3ABA), many potential sources of inhibitor–metal interaction can be recognized. The unshared pair of electrons present on two N atoms is of key importance in making coordinate bond with the metal. The π-electron cloud of the aromatic rings and the azomethine linkage also participate in the inhibition mechanism. Furthermore, the double bonds in the inhibitor molecule permit the back donation of metal d electrons to the π* orbital and this type of interaction cannot occur with amines [35]. This can be justified by the lower inhibition efficiency of the parent amine than that of Schiff base.
Table 4: Potentiodynamic polarization parameters of MS specimens in 1M HCl at 28°C in the absence and presence of 3FI3ABA

<table>
<thead>
<tr>
<th>Ecorr (mV/SCE)</th>
<th>Icorr (µA/cm²)</th>
<th>b1 (mV/dec)</th>
<th>b2 (mv/dec)</th>
<th>η_polar%</th>
<th>Rp (ohm)</th>
<th>η_bp%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>482</td>
<td>362</td>
<td>98</td>
<td>75</td>
<td>-</td>
<td>41.2</td>
</tr>
<tr>
<td>0.2</td>
<td>490</td>
<td>205</td>
<td>98</td>
<td>68</td>
<td>43.4</td>
<td>69.4</td>
</tr>
<tr>
<td>0.5</td>
<td>493</td>
<td>80</td>
<td>103</td>
<td>88</td>
<td>78.0</td>
<td>205.2</td>
</tr>
<tr>
<td>0.7</td>
<td>500</td>
<td>47</td>
<td>95</td>
<td>94</td>
<td>87.0</td>
<td>342.2</td>
</tr>
<tr>
<td>0.8</td>
<td>507</td>
<td>39</td>
<td>92</td>
<td>99</td>
<td>89.2</td>
<td>431.1</td>
</tr>
</tbody>
</table>

V. Conclusions

1. 3FI3ABA is a good inhibitor for MS in 1M HCl. A maximum of 95% of inhibition efficiency could be achieved with this inhibitor by gravimetric investigation.
2. Compared to the parent amine, 3-aminobenzoic acid, the Schiff base 3FI3ABA exhibited higher inhibition efficiency.
3. The inhibition mechanism is explained by adsorption. Adsorption of Schiff base on MS surface obey Langmuir isotherm.
4. The thermodynamic parameters of the adsorption are calculated from the adsorption isotherms which showed that both physisorption and chemisorption are involved in the inhibition process.

References

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