THE INHIBITION MILD STEEL CORROSION IN PHOSPHORIC ACID SOLUTIONS BY 2-PHENYL-1-HYDRAZINE CARBOXAMIDE

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ABSTRACT

In this work the effect of 2-phenyl-1-hydrazine carboxamide on the corrosion of mild steel in solutions of phosphoric acid (H₃PO₄) has been investigated in relation to the concentration of the inhibitor and acid, by weight loss, potentiodynamic polarization, and AC impedance (EIS) measurements. Results obtained revealed that this compound is a good mixed-type inhibitor. Increasing the acid concentration increased the metal corrosion but did not affect on the inhibitor efficiency. The optimum inhibitor concentration remained 150 ppm for various concentration of H₃PO₄. The surface morphologies of specimens after 1 hour of immersion in various solutions were studied by scanning electron microscopy (SEM). The Langmuir adsorption isotherm fitted well with the experimental data.

Keywords: Potentiodynamic; EIS; Inhibitor; SEM; Corrosion

INTRODUCTION

Phosphoric acid (H₃PO₄) has many important uses, especially in the production of fertilizers. Most of the acid is produced from phosphate rocks by the wet process based on the reaction between phosphate rocks and acid solutions. This acid (H₃PO₄) is a medium-strong acid, but it is still shows strong corrosiveness on ferrous or ferrous alloys. There is a great need to protect steel material used in the phosphoric acid industry from corrosion. Little work appears to have been done on the inhibition of steel in H₃PO₄ solutions. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. Compounds with functional groups containing hetero-atoms which can donate lone pair electrons are found to be particularly useful as inhibitors for corrosion of metals. Some organic compounds have been synthesized and investigated as inhibitors for corrosion of metals in acidic solutions. The goal of the present work was to study the inhibition characteristics of 2-phenyl-1-hydrazine carboxamide as corrosion inhibitor for mild steel in H₃PO₄ using different techniques such as weight loss, potentiodynamic polarization and AC impedance spectroscopy.

EXPERIMENTAL

Samples and solutions

Mild steel specimens having percent composition of 0.05C, 0.65Mn, 0.35Si, 0.01S, 0.01P and remaining Fe were used. Surface of specimens was mechanically polished on wet 240, 400, 600 abrasive paper (grades 300-1200), rinsed with distilled water, degreased with absolute ethanol and dried at room temperature before using. All used materials were extra pure and solutions were prepared by using distilled water.

Gravimetric studies

The specimens were used for gravimetric measurement had a rectangular form (1cm x 1cm x 0.1cm). The weight loss of specimens in various concentration of H₃PO₄ (1M, 2M, 3 M) with and without addition of different concentration of inhibitor after 1 hour of immersion period at 25°C was determined. The average three triplicate values was used according to the ASTM standard procedure described in literature.

Electrochemical measurements

For electrochemical studies, the cell used was a conventional three electrodes Pyrex glass with a platinum counter electrode and a standard calomel electrode (SCE) as reference. The working electrode was embedded in Teflon so that its cross-sectional area (1 cm²) was in contact with the solution. The electrochemical impedance experiments were carried out using AC signals of amplitude 5mV peak to peak at the open circuit potential (OCP) in the frequency range 100 kHz to 100mHz after 30 min immersion in the electrolyte cell. The impedance experiments were carried out with a Potentiostat/Galvanostat 263A (EG&G) Princeton Applied Research HF response model 1025. Pseudo-Polarization curves were recorded with scanning rate of 1 mV/s, after 30 min immersion from -700 to 0 mV vs. SCE at room temperature.

Scanning electron microscopy

The surface microstructure of specimens after 1 hour of immersion in various concentrations of H₃PO₄ with optimum concentration of inhibitor (150ppm) was studied by using SEM model CamScan MV2300.

RESULTS AND DISCUSSION

Weight loss

The inhibition efficiency of inhibitor (h%) in various concentration of H₃PO₄ was calculated as follows:

\[ \eta_w \% = \frac{\Delta W_0 - \Delta W}{\Delta W_0} \times 100 \]  

Where \( \Delta W_0 \) and \( \Delta W \) are the weight losses per unit area per time in the absence and presence of the inhibitor, respectively. The obtained data are summarized in Table 1.

Table 1. Inhibitor efficiencies from weight loss measurements.

<table>
<thead>
<tr>
<th>Inh.conc. (ppm)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>95.30</td>
</tr>
<tr>
<td>100</td>
<td>96.50</td>
</tr>
<tr>
<td>150</td>
<td>97.50</td>
</tr>
<tr>
<td>200</td>
<td>98.93</td>
</tr>
</tbody>
</table>

Table 1 shows the variation of inhibition efficiency percent (h%) with concentration of H₃PO₄ in presence and absence of various concentration of inhibitor. As seen, the inhibition efficiency increase with increasing inhibitor concentration to 150 ppm, in all Concentration of acid and the maximum (h%) was approximately 98.9%.

Potentiodynamic polarization

Fig 1 shows the polarization curves obtained for mild steel in various concentration of H₃PO₄ without inhibitor that indicated increasing mild steel corrosion by increasing acid concentration and fig 2 shows polarization curves in 2M H₃PO₄ without and with different concentration of inhibitor. It is clearly seen that this inhibitor shifted both the anodic and cathodic branches of polarization curves of the pure acid solution to lower values of current density indicating the inhibition of the both hydrogen evolution (HER) and mild steel dissolution reactions.
Fig 1. Polarization curves in different concentrations of H$_3$PO$_4$.

Fig 2. Polarization curves in 2M H$_3$PO$_4$ in absence and presence of various concentrations of inhibitor.

Table 2 gives the obtained parameters from polarization curves. The inhibition efficiency (η$_I$) of inhibitor was calculated by the following equation:

$$ \% \eta_I = \frac{I_0 - I}{I_0} \times 100 \quad (2) $$

Table 2. Polarization parameter values.

<table>
<thead>
<tr>
<th>%η</th>
<th>$I_{cor}$ $\mu$A/cm$^2$</th>
<th>$E_{cor}$ vs SCE/mv</th>
<th>Inh.conc./ppm</th>
<th>H$_3$PO$_4$ conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>430.500</td>
<td>-527.0</td>
<td>0</td>
<td>1M</td>
</tr>
<tr>
<td>99.20</td>
<td>3.439</td>
<td>-480.6</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>567.900</td>
<td>-525.3</td>
<td>0</td>
<td>2M</td>
</tr>
<tr>
<td>96.1</td>
<td>22.140</td>
<td>-492.3</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>98.0</td>
<td>11.358</td>
<td>-484.3</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>99.3</td>
<td>3.975</td>
<td>-486.9</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>99.0</td>
<td>5.679</td>
<td>-487.3</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1103.000</td>
<td>-517.0</td>
<td>0</td>
<td>3M</td>
</tr>
<tr>
<td>99.1</td>
<td>9.927</td>
<td>-474.5</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

Where $I_0$ and $I$ are the uninhibited and inhibited corrosion current densities determined by extrapolation of cathodic and anodic Tafel lines at 150 mV more positive and negative than $E_{cor}$.

Electrochemical impedance spectroscopy

Fig 3a shows the Nyquist plots of mild steel in 2M H$_3$PO$_4$ without and with various concentrations of inhibitor.

Table 2 shows the Nyquist plots of mild steel in 2M H$_3$PO$_4$. When 3M H$_3$PO$_4$ is added, the Nyquist plots are more distorted. The Nyquist plots are obtained by applying impedance spectroscopy technique.

The charge transfer resistance ($R_{ct}$) values are calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance ($C_d$) was obtained from the following equation:

$$ f \left( \frac{-Z''_{max}}{Z''_{min}} \right) = \frac{1}{2\pi f C_d R_{ct}} \quad (2) $$

F is the frequency at the apex of the semicircle in the Nyquist plot. Fig. 3b shows the Nyquist plots of mild steel in different concentrations of H$_3$PO$_4$ with optimum concentration of inhibitor. It was found that by increasing the concentration of H$_3$PO$_4$, the mild steel corrosion was constant. The inhibition efficiency percent (η$_I$) of inhibitor is calculated by the following equation:

$$ \eta_I = \frac{R_{ct} - R_{ct}^{o}}{R_{ct}^{o}} \times 100 \quad (3) $$
Where $R_{ct}$ and $R_{0ct}$ are the charge transfer resistance values with and without inhibitor, respectively. The impedance parameters derived from Nyquist plots are summarized in table 3.

Table 3. Obtained parameters from the Nyquist plots.

<table>
<thead>
<tr>
<th>%η</th>
<th>$C_d/\mu\text{Fcm}^2$</th>
<th>$R_{ct}/\Omega\text{cm}^2$</th>
<th>Inh.conc./ppm</th>
<th>$H_3\text{PO}_4$ conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>91.62</td>
<td>365.80</td>
<td>12.9</td>
<td>0</td>
<td>2M</td>
</tr>
<tr>
<td>97.75</td>
<td>78.12</td>
<td>154.1</td>
<td>50</td>
<td>2M</td>
</tr>
<tr>
<td>98.70</td>
<td>57.27</td>
<td>575.6</td>
<td>100</td>
<td>2M</td>
</tr>
<tr>
<td>98.40</td>
<td>73.25</td>
<td>995.2</td>
<td>150</td>
<td>2M</td>
</tr>
<tr>
<td>97.67</td>
<td>270.30</td>
<td>35.5</td>
<td>0</td>
<td>1M</td>
</tr>
<tr>
<td>98.66</td>
<td>388.90</td>
<td>55.91</td>
<td>150</td>
<td>1M</td>
</tr>
<tr>
<td>98.59</td>
<td>64.45</td>
<td>643.1</td>
<td>150</td>
<td>3M</td>
</tr>
</tbody>
</table>

From the Nyquist parameter values it was found that increasing $H_3\text{PO}_4$ concentration increases the mild steel corrosion respectively, and by increasing the inhibitor concentration increase $R_{ct}$ and decrease $C_d$ values. It is due to the adsorption of inhibitor on the metal surfaces and leads to protective film formation.

So it was found, that increasing concentration of $H_3\text{PO}_4$ did not affect on the inhibition efficiency of inhibitor, however, the optimum inhibitor concentration remained 150 ppm for various concentration of $H_3\text{PO}_4$. This result was similar to the results obtained from weight loss and potentiodynamic polarization methods.

**Scanning electron microscopy**

Micro structural studies of mild steel in various concentration of $H_3\text{PO}_4$ in absence and presence of optimum concentration of inhibitor were performed and were illustrated in fig.4.

It is clear that the corrosion attack was more pronounced in absence of the studied inhibitor, while the film formed on the metal surface becomes more protective, where the specimen surface is nearly intact as even the original polishing scratches are seen exposure.

**Adsorption isotherm**

The performance of the studied inhibitor ($2$-phenyl-1-hydrazone carboxamide) as a corrosion inhibitor may be attributed to the presence of electron donor groups ($N,O$ and aromatic ring) in the molecular structure of inhibitor, which favors the greater adsorption of it on the metal surface.

The unshared and $\pi$ electrons interact with $d$-orbital of steel to provide a protective film. To quantify the effect of inhibitor concentration on the corrosion rate, it is a common practice to fit the rate data to equilibrium adsorption expressions, such as the Langmuir equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C'$$  \hspace{1cm} (4)

Where $\theta$ is the fraction surfaces coverage by the inhibitor and $K_{ads}$ is the equilibrium constant for the adsorption reaction:

$$\theta = \frac{\eta \%}{100}$$  \hspace{1cm} (5)

The use of the Langmuir treatment is often justified with the argument that inhibition must involve adsorption. In this study, $C_{inh}$ is plotted against $C_{inh}$, a linear relationship is obtained for each media indicating the Langmuir behavior (fig.5).

![Fig 4. Surface features of mild steel exposed to various concentration of $H_3\text{PO}_4$ in absence and presence of optimum conc. of inhibitor.](image1)

![Fig 5. Langmuir plots for inhibitor on mild steel in various concentration of $H_3\text{PO}_4$.](image2)
CONCLUSIONS

2-phenyl-1-hydrazine carboxamide was a good inhibitor for mild steel in H3PO4 media. This inhibitor acted as mixed inhibitor and maximum efficiency (98%) attains an optimum value at 150 ppm in H2PO4, and the acid concentration did not affect on the optimum efficiency of inhibitor. The obtained results from different methods (EIS weight loss and polarization) were in good agreement. The adsorption of inhibitor was consistent with a Langmuir isotherm model. Micro structural studies elucidated a protective film on the metal surface in presence of inhibitor.

REFERENCES