Hexamine as Corrosion Inhibitors for Zinc in Phosphoric Acid

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Abstract: The corrosion of zinc in phosphoric acid containing hexamine has been studied at different acid concentrations, inhibitor concentration and temperatures. Corrosion increases with the concentration of acid and the temperature. The inhibition efficiency (IE) of hexamine increases with the concentration of inhibitor. The IE decreases with the increase in concentration of acid. As temperature increases, percentage of inhibition decreases. The plot of log (θ/(1-θ)) versus log C results in a straight line suggest that the inhibitors cover both the anodic and cathodic regions through general adsorption following Longmuir isotherm. Galvanostatic polarization curves show polarization of both anodes as well as cathodes.

Keywords: Corrosion, Zinc, Phosphoric acid, Hexamine.

Introduction

The problem of corrosion is of considerable importance, nowadays due to increase in uses of metals and alloys. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. Phosphoric acid is a major chemical product, which has uses many important especially in the production of fertilizers.

Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors\textsuperscript{13}. According to Hackerman et al.\textsuperscript{4} the inhibitive properties of a series of secondary aliphatic and cyclic amines in acid media are controlled by the percentage of π-orbital of free electron on the nitrogen atom of these compounds. Lin Wang et al.\textsuperscript{5} has studied the corrosion inhibition of zinc in phosphoric acid solution by 2–mercapto benzimidazole. Vashi et al. studied ethanolamines\textsuperscript{6} and ethylamines\textsuperscript{7} as corrosion inhibitors for zinc in phosphoric acid. Hexamine was reported as effective corrosion inhibitor for various metals in acid.\textsuperscript{8-10} In the present work, the corrosion of zinc by phosphoric acid containing isomer of hexamine has been reported.
Experimental

To study the corrosion of zinc in phosphoric acid, weight loss method, temperature effect, potential as well as polarization measurements have been used. Rectangular specimens (4.50 x 2.03 x 0.17 cm) of zinc having an area of 0.205 dm² were cleaned by buffing and immersed in 0.01, 0.05 0.10 and 0.15 M acid concentration with and without inhibitor containing 230 mL test solution at 301±1 K for 24 h duration period. After the test, specimens were cleaned by 10% chromic acid solution having 0.2% BaCO₃ for a period of about 2 minutes. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. Triplicate experiments were performed in each case and the mean value of weight loss was reported in form of corrosion rate. All chemicals used were of AR grade. The test solution was prepared in double distilled water.

To study the effect of temperature on corrosion of zinc in 0.05 M H₃PO₄, the specimens were immersed in 230 mL of corrosive solution and corrosion rate was determined at solution temperature of 303, 313, 323 and 333 K for an immersion period of 3 h with and without inhibitors.

For polarization study, metal specimens having an area of 0.0268 dm² were immersed in 230 ml corrosive solution without and with 80 mM inhibitor concentration in 0.01 M H₃PO₄. The test cell includes the metal specimen as a working electrode, corrosive solution in which the specimen was to be tested and saturated calomel electrode (SCE) as a reference electrode as well as Platinum electrode as an auxiliary electrode. The polarization study was made by using Potentio-Galvano-Scan (Weaving PGS 81) meter. Polarization curves were plotted with potential against log current density (called Tafel plots). Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (I_corr) and the corrosion potential (E_corr).

IE has been calculated as follows:

\[ \text{IE} \% = \left( \frac{(W_u - W_i)}{W_u} \right) \times 100 \]  

Where, \( W_u \) is the weight loss of metal in uninhibited acid and \( W_i \) is the weight loss of metal in inhibited acid. Energy of activation ( Ea) has been calculated from the slope of log \( \rho \) versus \( 1/T \) (\( \rho \) = corrosion rate, \( T \) = absolute temperature) and also with the help of the Arrhenius equation.

\[ \log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]  

Where, \( \rho_1 \) and \( \rho_2 \) are the corrosion rate at temperature \( T_1 \) and \( T_2 \) respectively. The value of heat of adsorption (Q_ads) were calculated by the following equation.

\[ Q_{ads} = 2.303 R [\log (\theta_2 / 1 - \theta_2) - \log (\theta_1 / 1 - \theta_1)] \times \frac{T_1 \cdot T_2}{T_2 - T_1} \]  

Where, \( \theta_1 \) and \( \theta_2 \) \([\theta = (W_u - W_i)/W_i]\) are the fractions of the metal surface covered by the inhibitors at temperature \( T_1 \) and \( T_2 \) respectively. The values of the free energy of adsorption (\( \Delta G_a \)) were calculated with the help of the following equation.

\[ \log C = \log (\theta / 1 - \theta) - \log B \]  

Where, \( \log B = -1.74 - (\Delta G_a / 2.303 RT) \) and \( C \) is the inhibitor concentration. The enthalpy of adsorption (\( \Delta H_{ads}^\circ \)) and entropy of adsorption (\( \Delta S_{ads}^\circ \)) are calculated using the equation.

\[ \Delta H_{ads}^\circ = E_a - RT \]  
\[ \Delta S_{ads}^\circ = \Delta H - \Delta G / T \]
Results and Discussion
The results are presented in Tables 1 & 2 and Figures 1 & 2. To assess the effect of corrosion of zinc in phosphoric acid, hexamine was added as inhibitor.

Figure 1. Plot of $\log(\theta / (1-\theta))$ versus $\log C$ for hexamine in 0.01 M phosphoric acid concentration

Figure 2. Polarization curves for corrosion of zinc in 0.01 M phosphoric acid containing 80 mM inhibitors

Corrosion in acid
The rate of corrosion increases with the increase in acid concentration. The corrosion rate was 365.2, 1887.6, 3580.9 and 5205.2 mg/dm$^2$ in 0.01, 0.05, 0.10 and 0.15 M $\text{H}_3\text{PO}_4$ concentrations respectively for a period of 24 h at 301±1 K as shown in Table 1.

Effect of inhibitor concentration
The IE of the hexamine increases with the inhibitor concentration, e.g. in case of hexamine in 0.01 M $\text{H}_3\text{PO}_4$ the IE was found to be 88.0, 94.7, 97.3 and 98.7% with respect to 20, 40, 60 and 80 mM inhibitor concentration respectively (Table 1).

Effect of acid concentration
The IE decreases with the increase in acid concentration. At 80 mM inhibitor concentration, the IE of hexamine was 98.7, 97.4, 93.3 and 88.5% with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration respectively Table 1.
Table 1. Corrosion rate (CR) and inhibition efficiency (IE) of zinc in 0.01, 0.05, 0.10 and 0.15 M H₃PO₄ acid containing hexamine as inhibitors for an immersion period of 24 h at 301±1 K

<table>
<thead>
<tr>
<th>System</th>
<th>Conc. of Inhibitor (mM)</th>
<th>0.01 Acid concentration, M</th>
<th>0.05</th>
<th>0.10</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CR (mg/dm²) IE (%)</td>
<td>CR (mg/dm²) IE (%)</td>
<td>CR (mg/dm²) IE (%)</td>
<td>CR (mg/dm²) IE (%)</td>
<td>CR (mg/dm²) IE (%)</td>
</tr>
<tr>
<td>A</td>
<td>--</td>
<td>365.2</td>
<td>1887.6</td>
<td>3580.9</td>
<td>5205.2</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>43.8</td>
<td>88.0</td>
<td>628.1</td>
<td>66.7</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>19.5</td>
<td>94.7</td>
<td>131.5</td>
<td>93.0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>9.7</td>
<td>97.3</td>
<td>68.2</td>
<td>96.4</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>4.9</td>
<td>98.7</td>
<td>48.7</td>
<td>97.4</td>
</tr>
</tbody>
</table>

Effect of temperature

In 0.05 M H₃PO₄ corrosion rate increases as temperature increases i.e. corrosion rate was 832.6, 993.3, 1193.0 and 1314.7 mg / dm² for 3 h immersion period. Inhibition efficiency was found to decrease with temperature. The IE for hexamine at 80 mM concentration was 98.8, 98.5, 98.3 and 97.7 % at 303, 313, 323 and 333 K respectively for 3 h immersion period.

Value of Ea calculated from eq.2 was found to be higher (30.8 kJ mol⁻¹) than that of uninhibited system (12.7 kJ mol⁻¹). This suggests that the presence of reactive centres on the inhibitor can block the active sites for corrosion, resulting in an increase in Ea. The values of Ea calculated from the slope of Arrhenius plot and using eq.2 are almost similar. It was evident that in all cases, the Q_ads values were negative and ranging from −28.0 to-9.3 kJ mol⁻¹. Oguzie explained that the negative values of Q_ads also signify that the degree of surface coverage decreased with rise in temperature.

The mean ∆Ga values was -28.2 kJ mol⁻¹. This suggests that they are strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji. The enthalpy changes (∆Hₐ) was positive (28.2 kJ mol⁻¹) indicating the endothermic nature of the reaction suggesting that higher temperature favours the corrosion process. Adeyen described that if the ∆H < 10 kJ mol⁻¹ the adsorption is probably physisorption and if the ∆H > 10 kJ mol⁻¹ values indicate that the hexamine strongly adsorbed on zinc is chemisorption. The entropy (∆S_ads) values was positive (0.18 kJ mol⁻¹) confirming that the corrosion process is entropically favourable.

Polarization behaviour

Anodic and cathodic galvanostatic polarization curves for zinc in 0.01 M H₃PO₄ acid, alone and containing 80 mM concentration of hexamine is shown in Figure 2. The curves show polarization of both, the cathodes as well as anodes. IE calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines are given in Table 2. The IE calculated from Tafel plots agree well (within ± 0.2%) with the values obtained from weight loss data.

Table 2. Polarisation data and inhibition efficiency (IE) of hexamine for zinc in 0.01 M H₃PO₄ at 301±1 K, Inhibitor concentration: 80 mM, Effective area of specimen = 0.0268 dm²

<table>
<thead>
<tr>
<th>System</th>
<th>E_corr (mV)</th>
<th>CD (mA/cm²)</th>
<th>Tafel slope (mV/decade)</th>
<th>IE (%) from methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-940</td>
<td>0.560</td>
<td>88</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>-995</td>
<td>0.006</td>
<td>415</td>
<td>98.7</td>
</tr>
</tbody>
</table>

A = H₃PO₄, B = H₃PO₄ + Hexamine, βₐ = Anodic Tafel constant, βₖ = Cathodic Tafel constant, \( \beta = (\betaₐ \times \betaₖ)/[2.3 (Bₕ + \betaₖ)] \) CD = Corrosion current density from intersection of anodic and cathodic lines.
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**Mechanism of corrosion**

Generally, zinc dissolve in phosphoric acid solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{(anodic reaction)} \quad (7) \]

Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.

\[ 2\text{H}^+ + 2e^- \rightarrow 2\text{H} \quad \text{(cathodic reaction)} \quad (8) \]

or \( \text{H} + \text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_2 \uparrow + \text{H}_2\text{O} \quad (9) \)

The mechanism of inhibitor of corrosion is believed to be due to the formation and maintenance of a protective film on the metal surface. Further, when \( \log (\theta / (1-\theta)) \) is plotted against \( \log C \) straight line was obtained (Figure 1). This suggests that the inhibitor cover both the anodic as well as cathodic regions through general adsorption following Langmuir adsorption isotherm.

![Scheme 1. Structure of hexamine](image)

Macro molecular size and higher number\(^{21}\) of \( N \)-atoms of hexamine (Scheme 1) might have covered almost all active source of zinc. Four nitrogen atom of the hexamine having high electron density must have functioned as the reaction center\(^{22}\) and the hexamine molecules might have been chemisorbed to form a thin monolayer on the zinc surface.

Hexamine (hexamethylenetetramine) consists of four nitrogen atoms and six \( \text{CH}_2 \) groups. Because of the presence of three nitrogen atoms electrons are disposed easily in the ring and therefore it is expected to be an effective inhibitor. The inhibitor action can be accounted by the interaction of lone pair of electrons in the nitrogen atom on the positively charged metal surface. The presence of six methylene groups also helps to lead to an enhancement of electron density at the nitrogen atom, which enhances its adsorption on the metal surface. This in turn leads to an increase in the value of IE.

The protective effect of the inhibitor is probably due to formation of an insoluble film\(^{23}\). Hence the mechanism of the inhibitive action is possibly due to the blocking of anodic and cathodic sites by adsorption, which enables the formation of a protective insoluble film.

**Conclusion**

- As the acid concentration increase the corrosion rate increases and IE of inhibitor decreases.
- At all concentration of acid, as the inhibitor concentration increases IE increases and corrosion rate decreases.
- Mean value of \( \text{Ea} \) in inhibited acid are higher than the value of \( \text{Ea} \) in acid only, which shows that chemisorptions of the inhibitor molecule.
• As the temperature increases corrosion rate increases while IE decreases.
• Hexamine act as mixed type of inhibitor.

Acknowledgment
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References