ANISIDINE ISOMERS AS CORROSION INHIBITORS
FOR ZINC IN HYDROCHLORIC ACID

Vashi R. T.* and Desai Krunal
Department of Chemistry, Navyug Science College, Surat (INDIA)

ABSTRACT
The corrosion of zinc in hydrochloric acid containing anisidines has been studied at different acid concentration and temperature. Corrosion increases with increase of acid concentration and temperature. As concentration of acid increases corrosion rate increases while Inhibition Efficiency (I.E.) of anisidines decreases. As concentration inhibitor increases I.E. also increases. At 20 mM inhibitor concentration in 0.01 M HCl at 301\textdegree K for 24 h immersion period, the efficiency of inhibitors decreases in the order: o-anisidine (98.35 %) > p-anisidine (97.80 %) > m-anisidine (96.71 %). As the temperature increases, the value of $\Delta G^o_a$ increases, while percentage of inhibition decreases. The mode of inhibition action appears to be chemisorption since the plot of $\log (\theta / 1-\theta)$ versus log C gave a straight line, which suggested that the inhibitors covered both the anodic and cathodic regions through general adsorption following the Langmuir isotherm. Anodic and cathodic galvanostatic polarisation curves show polarization of both anode and cathode.

Key Words: Corrosion, Zinc, Hydrochloric Acid, Anisidines, Galvanostatic polarization

INTRODUCTION
Corrosion is a process that occurs when a material deteriorates due to its interaction with the surrounding environment in which an electrochemical reaction consumes the material through oxidation. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. Zinc corrodes in solution having pH lower than 6.0 and higher than 12.5, while within this range the corrosion is very slow. Hydrochloric acid is highly corrosive, strong mineral acid since it is completely dissociated in water and has major industrial uses. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors. P. S. Desai and S. M. Kapopara studied the inhibiting effect of anisidines on corrosion of aluminium in hydrochloric acid. N. Haldar et al. studied anisidine isomers as a corrosion inhibitor for oil well casting steel in hydrochloric acid. R.T.Vashi et al. studied anisidines as corrosion inhibitors for zinc in phosphoric acid.

AIMS AND OBJECTIVES
In the present study, the corrosion of zinc in hydrochloric acid in absence and presence of anisidines as inhibitors has been reported. Inhibition efficiency of inhibitors were compared by weight loss method and polarization method.

MATERIAL AND METHODS
Weight loss measurement
To study the corrosion of zinc in hydrochloric acid, weight loss method, temperature effect, potential as well as polarization measurements have been used. Rectangular specimens (4.65 x 2.15 x 0.16 cm) of zinc having an area of 0.2221 dm$^2$ were taken and cleaned by buffing and immersed in 0.01, 0.05, 0.10 and 0.15 M HCl concentration with and without inhibitor containing 230 ml test solution at 301 + 1 K for 24 h immersion period. After the test, specimens were cleaned by 10% chromic acid solution having 0.2 % BaCO$_3$ for a period of about 2 minutes. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. The mean value of weight loss was reported as mg/dm$^2$ shown in Table 1. All chemicals used were of AR grade. The corrosive solution was prepared in double distilled water.

Temperature effect
To study the effect of temperature on corrosion of zinc in 0.05 M HCl, the specimens were
immersed in 230 ml of corrosive solution and corrosion loss was determined at solution temperature of 303, 313, 323 and 333 K for an immersion period of 2 h with and without inhibitors. From the data I.E., energy of activation (Ea), heat of adsorption (Qads), free energy of adsorption (ΔGads), change of enthalpy (ΔH) and entropy of adsorption (ΔS) were calculated and shown in Table 2.

Polarization method
For polarization study, metal specimens having an area of 0.02 dm² were immersed in 230 ml corrosive solution without and with 20 mM inhibitor concentration in 0.01 M HCl. 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 potentiostat / galvanostat make Gamry, USA with inbuilt corrosion software. Polarization curves were plotted with potential against log current density (called Tafel plots). Cathodic and anodic polarization curves give cathodic and anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (Icorr) and the corrosion potential (Ecorr).

RESULTS AND DISCUSSION
The results are presented in Tables 1 to Table 3 and Fig. 1 to Fig 3. To assess the effect of corrosion of zinc in hydrochloric acid, anisidines were added as inhibitors. I.E. has been calculated as follows:

\[ I.E. (\%) = \left( \frac{(W_u - W_i)}{W_u} \right) \times 100 \]  

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:

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

Where, \( \rho_1 \) and \( \rho_2 \) are the corrosion rate at temperature \( T_1 \) and \( T_2 \) respectively.

The value of heat of adsorption (Qads) was calculated by the following equation:

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

where, \( \theta_1 \) and \( \theta_2 \) \([= (W_u - Wi)/W_u] \) 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 (ΔGads) were calculated with the help of the following equation:

\[ \log C = \log \left( \frac{\theta}{1 - \theta} \right) - \log B \]  

Where, log B = -1.74 – (ΔGa / 2.303 RT) and C is the inhibitor concentration.

The enthalpy of adsorption (ΔHads) and entropy of adsorption (ΔSads) are calculated using the equation:

\[ \Delta H_{ads} = E_a - RT \]  

\[ \Delta S_{ads} = \Delta H - \Delta G / T \]  

Corrosion in acid
The corrosion rate increases with the increase in concentration of acid. The corrosion rate was 81.98, 1136.48, 3151.05 and 5221.85 mg/dm² in 0.01, 0.05, 0.10 and 0.15 M HCl concentrations respectively for a period of 24 h at 301 ± 1 K as shown in Table 1.

Corrosion in presence of inhibitors
To assess their protective value anisidines were added in 5, 10, 15 and 20 mM concentration in 0.01, 0.05, 0.10 and 0.15 M HCl concentrations for 24 h duration period (Table 1).

Effect of inhibitor concentration
At constant acid concentration, the I.E. of the anisidines increases with the inhibitor concentration, e.g. in case of o-anisidine in 0.01 M HCl the I.E. was found to be 93.96, 95.61, 96.71 and 98.35 % with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration respectively (Table 1).

Effect of acid concentration
At constant inhibitor concentration, the I.E. decreases with the increase in acid concentration. At 20 mM inhibitor concentration, the I.E. of m-anisidine is 96.71, 95.56, 79.85 and 59.21 % with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration respectively (Table 1).

Effect of temperature
As the temperature increases, corrosion rate increases while percentage of I.E. decreases...
Table 1: Corrosion Rate and Inhibition Efficiency of zinc in 0.01, 0.05, 0.10 and 0.15 M HCl containing anisidines as inhibitors for an immersion period of 24 h at 301 ± 1 K

<table>
<thead>
<tr>
<th>System</th>
<th>Inhibition Concentration</th>
<th>Acid concentration</th>
<th>0.01 M</th>
<th>0.05 M</th>
<th>0.10 M</th>
<th>0.15 M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mM</td>
<td>mg/dm²</td>
<td>%</td>
<td>mg/dm²</td>
<td>%</td>
<td>mg/dm²</td>
</tr>
<tr>
<td>A</td>
<td>--</td>
<td>81.98</td>
<td>1136.48</td>
<td>3151.05</td>
<td>5221.85</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>4.95</td>
<td>93.96</td>
<td>274.20</td>
<td>75.87</td>
<td>1433.58</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.60</td>
<td>95.61</td>
<td>231.87</td>
<td>79.60</td>
<td>998.64</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.70</td>
<td>96.71</td>
<td>128.32</td>
<td>88.71</td>
<td>775.77</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.35</td>
<td>98.35</td>
<td>37.82</td>
<td>96.67</td>
<td>585.32</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>6.75</td>
<td>91.77</td>
<td>291.31</td>
<td>74.37</td>
<td>1449.79</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.30</td>
<td>92.32</td>
<td>279.15</td>
<td>75.44</td>
<td>1090.95</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>5.40</td>
<td>93.41</td>
<td>119.76</td>
<td>89.46</td>
<td>1001.80</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2.70</td>
<td>96.71</td>
<td>50.42</td>
<td>95.56</td>
<td>634.85</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>8.10</td>
<td>90.12</td>
<td>303.01</td>
<td>73.34</td>
<td>1468.25</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.95</td>
<td>93.96</td>
<td>274.65</td>
<td>75.83</td>
<td>1009.90</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.60</td>
<td>95.61</td>
<td>140.92</td>
<td>87.60</td>
<td>907.69</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.80</td>
<td>97.80</td>
<td>45.47</td>
<td>96.00</td>
<td>644.30</td>
</tr>
</tbody>
</table>

A = HCl, B = HCl + o-anisidine, C = HCl + m-anisidine, D = HCl + p-anisidine
### Table 2: Effect of temperature on Corrosion Rate, Inhibitive Efficiency (%), energy of activation (heat of adsorption, $Q_{ads}$) and free energy of adsorption ($\Delta G^*_a$) for zinc in 0.05 M HCl containing anisidines

Inhibitor concentration = 20 mM  
**Immersion period = 2 h**  
**Effective area of specimen = 0.2221 dm$^2$**

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature, K</th>
<th>Mean $E_a$ from Arrhenius</th>
<th>$Q_{ads}$ (kJ mol$^{-1}$)</th>
<th>Mean Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303</td>
<td>313</td>
<td>323</td>
<td>333</td>
</tr>
<tr>
<td>A</td>
<td>773.9</td>
<td>-</td>
<td>949.1</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>9.5</td>
<td>98.8</td>
<td>40.1</td>
<td>95.8</td>
</tr>
<tr>
<td>C</td>
<td>22.5</td>
<td>97.1</td>
<td>48.2</td>
<td>94.9</td>
</tr>
<tr>
<td>D</td>
<td>14.4</td>
<td>98.1</td>
<td>44.6</td>
<td>95.3</td>
</tr>
</tbody>
</table>

$A = HCl, B = HCl + o$-anisidine, $C = HCl + m$-anisidine, $D = HCl + p$-anisidine,

### Table 3: Polarisation data and Inhibition Efficiency (I.E.) of anisidines for zinc in 0.01 M HCl at 301 ± 1 K

Inhibitor concentration: 20 mM; Effective area of specimen = 0.02 dm$^2$

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{corr}$ mV</th>
<th>CD</th>
<th>Tafel slope (mV/decade)</th>
<th>B(mV)</th>
<th>I.E. (%) from methods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{corr}$ mA/cm$^2$</td>
<td>Anodic</td>
<td>Cathodic</td>
<td>Weight loss</td>
<td>By polarization</td>
</tr>
<tr>
<td>A</td>
<td>-1040</td>
<td>0.1190</td>
<td>36.36</td>
<td>277.77</td>
<td>13.96</td>
</tr>
<tr>
<td>B</td>
<td>-1060</td>
<td>0.0049</td>
<td>90.00</td>
<td>130.00</td>
<td>23.12</td>
</tr>
<tr>
<td>C</td>
<td>-1070</td>
<td>0.0075</td>
<td>122.22</td>
<td>166.66</td>
<td>30.65</td>
</tr>
<tr>
<td>D</td>
<td>-1130</td>
<td>0.0065</td>
<td>15.55</td>
<td>21.05</td>
<td>3.88</td>
</tr>
</tbody>
</table>

$A = HCl, B = HCl + o$-anisidine, $C = HCl + m$-anisidine, $D = HCl + p$-anisidine, $\beta_a$ = Anodic Tafel constant, $\beta_c$ = Cathodic Tafel constant.

CD = Corrosion current density from interception of anodic and cathodic lines.
Mean ‘Ea’ values were calculated by using eq.2 for zinc in 0.05 M HCl is 29.2 kJ mol\(^{-1}\) while in acid containing inhibitor, the mean Ea values were found to be higher than that of uninhibited system (58.8 to 80.1 kJ mol\(^{-1}\)) (Table 2). The higher values of mean Ea indicate physical adsorption of the inhibitors on metal surface. The values of Ea calculated from the slope of Arrhenius plot (Fig. 2) and using eq. 2 were almost similar. From Table 2, it is evident that in all cases, the \(Q_{ad}\) values are negative and ranging from -8.2 to -100.3 kJ mol\(^{-1}\). The mean \(\Delta G_a\) values are negative almost in all cases and lie in the range of -28.3 to -29.3 kJ mol\(^{-1}\). This suggests that they are strongly adsorbed on the metal surface. The enthalpy changes (\(\Delta H^\circ_a\)) are positive (56.2 to 77.5 kJ mol\(^{-1}\)) indicating the endothermic nature of the reaction suggesting that higher temperature favors the corrosion process. The entropy (\(\Delta S^\circ_a\)) values are positive (0.27 to 0.35 kJ mol\(^{-1}\)) confirming that the corrosion process is entropically favourable.

**Mechanism of corrosion inhibition**

Generally, zinc dissolve in hydrochloric 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.

\[
2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2(\text{ads.}) \quad (\text{cathodic reaction}) \quad (8)
\]

or \[\text{H} + \text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_2 \uparrow + \text{H}_2\text{O}\]

or \[\text{H}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}\]

The de-localized \(\pi\)-electrons of these inhibitors facilitate its strong adsorption on the zinc surface leading to the outstanding corrosion inhibition. In addition, the oxygen of the methoxy group (-OCH\(_3\)) may facilitates the complexation to the zinc surface and helps to enhance the adhesion of anisidine coating to the zinc surface. The presence of –OCH\(_3\) group (i.e. an electron donating effect) will enhance the electron density by their inductive or mesomeric effect (Fig. 4).

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 lines are obtained in the case of inhibitor used (Fig. 1). This suggests that the inhibitor cover both the anodic as well as cathodic regions through general adsorption following Langmuir isotherm.

**Polarization behaviour**

Anodic and cathodic galvanostatic polarization curves for zinc in 0.01 M HCl acid, alone and containing 20 mM concentration of anisidines are shown in Fig. 3. The curves show polarization of both, the cathodes as well as anodes. I.E. calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines are given in Table 3. In almost all the cases, the I.E. from Tafel plots agree well (within ± 4 %) with the values obtained from weight loss data.

![Fig. 1: Plot of log (\(\theta /1-\theta\)) versus log C for anisidines in 0.05 M HCl concentration](image-url)
Fig. 2: Arrhenius plots for corrosion of zinc in 0.05M HCl in presence of 20 mM inhibitor concentration

Fig. 3: Polarization curve for corrosion of zinc in absence and presence of 20 mM concentration of inhibitors in 0.01 M HCl

Fig. 4: Mechanism of inhibitor of corrosion
CONCLUSION
As the acid concentration increases the corrosion rate increases while I.E. decreases. I.E. of all inhibitors decreases as the concentration of acid increases. As the inhibitor concentration increases the corrosion rate decreases and I.E. increases. Addition of inhibitors in corrosive media indicates that as the temperature increases corrosion rate increases while I.E. decreases. Inhibitors acts as mixed type of inhibitors.

ACKNOWLEDGEMENT
The authors are thankful to Department of Chemistry, Navyug Science College, Surat, India for providing laboratory facilities.

REFERENCES