Inhibiting effect of anisidines on corrosion of aluminium in hydrochloric acid

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Anisidines (o-, m- and p-) were used as corrosion inhibitors for aluminium in hydrochloric acid solution. The inhibition efficiency depended on the concentration and type of the anisidine. The inhibition efficiency ranged between 76 and 93% at the highest concentration (80 mM), and between 65 and 85% at the lowest concentration (20 mM) of inhibitor in 0.4 M HCl solution. Inhibition efficiency decreased with rise in temperature, this corresponded to surface coverage of the metal by the inhibitor. The calculated degrees of surface coverage, $\theta$, were found to increase with the inhibitor concentration. The results also showed that, the inhibitors were adsorbed on the aluminium surface according to Langmuir adsorption isotherm. Polarization study revealed that all the three anisidines functioned as slightly anodic but significantly cathodic inhibitors.

Keywords: Corrosion, Aluminium, Hydrochloric acid, Anisidine

Aluminium and its alloy show high resistivity towards a wide variety of corrosive environments. This may be due to the formation of a protective, tightly adherent invisible oxide film on the metal surface. The film is generally stable in solutions of $pH$ 4.5-8.5. However, due to the solubility of the film in strong acid and strong alkaline media, the metal shows high rate of corrosion under such conditions. Hydrochloric acid solutions are normally used for pickling of aluminium and for its chemical and electrochemical etching; processes that often lead to substantial dissolution of the metal. Acid solutions mainly HCl and H$_2$SO$_4$ are routinely used for the removal of undesirable scale and rust in several industrial processes. For this reason some sorts of inhibitors are generally used to control metal dissolution as well as acid consumption. Most of the well-known inhibitors which are organic compounds containing polar nitrogen, oxygen or sulphur atoms in a conjugated system have been reported to exhibit significant corrosion inhibiting efficacy. The efficiency of N-organic compounds as corrosion inhibitors depends on the possibility of the transfer of one pair of electrons from the organic compounds and formation of coordinate bonds with the metal or alloys. Therefore, the inhibition efficiency strongly depends on the structure and chemical properties of the layers that are formed under the particular experimental condition. Nitrogen containing organic compounds have been extensively used as corrosion inhibitors for the corrosion of metals like Cu and Zn in acid solutions. However, there is very little information about the inhibition of aluminium corrosion in HCl solutions using such organic compounds. Recently Umreon et al. have studied the corrosion and inhibition behaviour of aluminium in HCl in the absence and presence of inhibitors like polyvinyl pyrrolidone, polyacrylamide and their blends using weight loss and hydrogen evolution technique. The purpose of the present work is to investigate the effect of o-, m- and p-anisidine on the corrosion of aluminium in HCl solution using gravimetric and galvanostate polarization techniques.

**Experimental Procedure**

**Metal specimen**

Aluminium sheets of the 2S type aluminium (Al = 99.489; Fe = 0.348; Cr = 0.080; Mn = 0.024; Ti = 0.023; Zn = 0.021 and Cu = 0.015%) were used in this study. Each sheet having 0.22 cm thickness, was mechanically press-cut into coupons of dimension 2 x 5 cm with small hole of about 5 mm diameter near the upper edge. These coupons were used as such without further polishing, but were degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use.

**Reagents**

All chemicals and reagents used were of analytical grade and used as received without further purification. Aqueous HCl solutions (0.4, 0.5 and 0.6 M) were used as the aggressive media. Anisidines were used as inhibitors in the concentration range 20 to 80 mM.
Weight loss method
The test specimens were immersed in 0.4, 0.5 and 0.6 M HCl solution with and without inhibitors. Only one specimen was suspended by a glass hook, in each beaker containing 230 mL of the test solution and was open to air at room temperature for 24 h. After the immersion period, the specimens were cleaned with chromic-phosphate mixture solution, dried and weighed. Triplicate experiments were performed in each case and the calculated mean values of the weight loss data are presented in Table 1.

To study the effect of temperature on corrosion rate, the specimen were immersed in 230 mL of 0.5 M HCl solution with various anisidines as inhibitor having concentration 20, 40, 60, and 80 mM at solution temperatures of 313, 323 and 333 K for a period of 2 h. To study the effect of temperature, thermostat assembly with accuracy of ± 0.5°C was used.

Inhibition efficiency (η%), energy of activation (E_a), heat of adsorption (Q_ads) free energy of adsorption (ΔG^0_ads), enthalpy of adsorption (ΔH^0_ads) and entropy of adsorption (ΔS^0_ads) were calculated.

Polarization studies
For polarization study, metal specimens of rectangular design having an area of 0.0932 dm^2 were exposed to corrosive solutions. Aluminium was used as a working electrode, SCE was used as reference electrode and auxiliary graphite electrode was placed in 350 mL of corrosive media through which external current was supplied automatically from computerized polarization instrument. The change in potential was measured by potentiostate/galvanostate (Gamry-Make, USA) on potentiostate mode with 5 mV/s scan rate. Polarization study was done with and without inhibitors in 0.4 M HCl.

Results and Discussion
The results are presented in Tables 1 to 4 and Figs 1 to 3. The effect on corrosion of aluminium in HCl containing anisidine inhibitors was assessed.

Specific conductivity of solutions containing 0.4, 0.5 and 0.6 M HCl were found to be 109.0 × 10^{-3}, 122.3 ×10^{-3} and 123.60 × 10^{-3} mohs/cm respectively. This suggested that, specific conductivity increased with increase of acid concentration. The addition of inhibitors caused decrease in the specific conductivity. Specific conductivity for o-, m- and p-anisidines at 20 mM inhibitor concentration in 0.4 M acid concentration has been found to be 106.40 × 10^{-3}, 96.80 ×10^{-3} and 87.80 ×10^{-3} milimohs/cm respectively.

The corrosion rate of aluminium in HCl was increased with the acid concentration (Table 1). The inhibition efficiency (η%) and degree of surface coverage (θ) at each concentration of anisidine were calculated by comparing the corrosion loss in the absence (W_u) and presence of anisidine (W_i) using the relationships:

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

Table 1—Effect of acid concentration on weight loss (WL) and corrosion inhibition efficiency (η%) of anisidines for aluminium in HCl.

<table>
<thead>
<tr>
<th>Inhibitor conc. (mM)</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>807.88</td>
<td>-</td>
<td>1704.18</td>
</tr>
<tr>
<td>o-Anisidine</td>
<td>20</td>
<td>209.00</td>
<td>76.13</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>176.85</td>
<td>78.11</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>144.69</td>
<td>82.09</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>124.60</td>
<td>84.58</td>
</tr>
<tr>
<td>m-Anisidine</td>
<td>20</td>
<td>281.35</td>
<td>65.18</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>269.29</td>
<td>66.67</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>209.00</td>
<td>74.13</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>192.93</td>
<td>76.12</td>
</tr>
<tr>
<td>p-Anisidine</td>
<td>20</td>
<td>120.58</td>
<td>85.07</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>64.31</td>
<td>92.04</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>60.29</td>
<td>92.54</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>56.27</td>
<td>93.03</td>
</tr>
</tbody>
</table>
At constant inhibitor concentration, the inhibition efficiency decreased with the increase in acid concentration. At 80 mM inhibitor concentration, the inhibition efficiency of p-anisidine was 93.03, 89.15 and 85.69% with respect to 0.4, 0.5 and 0.6 M acid concentrations respectively. At constant acid concentration, the inhibition efficiency of the anisidine increased with the inhibitor concentration, e.g., with p-anisidine in 0.4 M HCl the inhibition efficiency was found to be 85.07, 92.04, 92.54 and 93.03% with respect to 20, 40, 60 and 80 mM inhibitor concentrations respectively (Table 1).

Temperature had significant influence on the metal corrosion rates. The effect of change in temperature on the corrosion rates of aluminum in 0.5 M HCl was examined. It was found that, the corrosion of aluminum increased with increase in temperatures (Table 2). At constant inhibitor concentration of 80 mM p-anisidine concentration, the inhibition efficiency was found to be 93.87, 87.50 and 77.67% at 313, 323 and 333 K respectively (Table 2).

In the present study general type of corrosion occurs predominately and less pitting. Plotting of \(\log(\theta/1-\theta)\) versus \(\log C\) resulted into straight lines indicating that the adsorption of the added inhibitors followed the Langmuir adsorption isotherm (Fig. 1). Therefore, adsorption of these compounds may be assumed to occur uniformly over the metal surface.

The values of the free energy of adsorption (\(\Delta G_{ads}^0\)) were calculated with slope of the following equation

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

where \(\log B=-1.74-\frac{\Delta G^0}{2.303RT}\) and \(C\) is the inhibitor concentration. The mean \(\Delta G_{ads}^0\) values are negative almost in all cases and lie in the range of -17.35 to -22.98 kJ. mol\(^{-1}\) (Table 3). The most efficient inhibitor showed more negative \(\Delta G_{ads}^0\) value. This suggested that, the test inhibitors were strongly adsorbed on the metal surface. The values of heat of adsorption (\(Q_{ads}\)) were calculated by the following equation.

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

From Table 3, it is evident that in all cases, the \(Q_{ads}\) values are negative and are in the range -8.53 to -120.51 kJ.mol\(^{-1}\). The negative values show that the adsorption, and hence the inhibition efficiency, decreases with an increase in temperature\(^{16}\).

Mean \(E_a\) value calculated by using Eq. (5) for aluminum in 0.5 M HCl is 30.97 kJ.mol\(^{-1}\) while in acid containing inhibitor, the mean \(E_a\) values are found to be higher than that of uninhibited system (Table 3). The higher values of mean \(E_a\) indicated physical adsorption of the inhibitors on metal surface\(^9\), which

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**Table 2—Effect of temperature on Weight Loss (WL) inhibitive efficiency (\(\eta\)%), for aluminium in 0.5 M HCl containing 80 mM inhibitor concentration.**

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature (K)</th>
<th>WL (mg/dm²)</th>
<th>I. E (%)</th>
<th>WL (mg/dm²)</th>
<th>I. E (%)</th>
<th>WL (mg/dm²)</th>
<th>I. E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313</td>
<td></td>
<td></td>
<td>323</td>
<td></td>
<td>333</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>204.97</td>
<td>-</td>
<td>321.52</td>
<td>-</td>
<td>413.95</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>68.32</td>
<td>66.67</td>
<td>136.64</td>
<td>57.50</td>
<td>265.25</td>
<td>35.92</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>56.27</td>
<td>72.55</td>
<td>156.74</td>
<td>51.25</td>
<td>289.37</td>
<td>30.10</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>12.56</td>
<td>93.87</td>
<td>40.19</td>
<td>87.50</td>
<td>92.44</td>
<td>77.67</td>
<td></td>
</tr>
</tbody>
</table>

\(A = \text{HCl}, B = \text{HCl+}\ \omega-\text{anisidine}, C = \text{HCl+}\ \mu-\text{anisidine}, D = \text{HCl+}\ \pi-\text{anisidine}\)

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**Fig. 1—Plot of log (\(\theta/1-\theta\)) versus log C for anisidines in 0.5 M HCl.**

\[
\theta = \left(\frac{W_a - W_i}{W_i}\right)
\]  

\(… (2)\)
leads to an increase in the energy barrier for the corrosion process. The values of $E_a$ calculated from the slope of Arrhenius plot (Fig. 2) and using Eq. (5) are almost similar. Energy of activation ($E_a$) has been calculated from the slopes of log $P$ versus $1/T$ ($P = \text{corrosion rate, } T = \text{absolute temperature}$) and also with the help of Arrhenius equation.

$$\log \frac{P_2}{P_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$ \hspace{1cm} \text{(5)}$$

where $P_1$ and $P_2$ are the corrosion rates at temperatures $T_1$ and $T_2$ respectively. The enthalpy of adsorption ($\Delta H^0_{\text{ads}}$) and entropy of adsorption ($\Delta S^0_{\text{ads}}$) were calculated using the following Eqs (6) and (7).

$$\Delta H^0_{\text{ads}} = E_a - RT$$ \hspace{1cm} \text{(6)}

$$\Delta S^0_{\text{ads}} = \frac{\Delta H^0_{\text{ads}} - \Delta G^0_{\text{ads}}}{T}$$ \hspace{1cm} \text{(7)}$$

The enthalpy changes ($\Delta H^0_{\text{ads}}$) are positive indicating the endothermic nature of the reaction suggesting that higher temperature favours the corrosion process. The entropy ($\Delta S^0_{\text{ads}}$) values are positive confirming that the corrosion process is entropically favourable.

Anodic and cathodic polarization curves for aluminium in 0.4 M HCl at 80 mM inhibitor concentration in the presence and absence of inhibitors are shown in Fig. 3. The values of the corrosion potential in presence of inhibitors were found to be more negative than those without inhibitors. Polarization study revealed that the inhibitors functioned slightly anodic but significantly cathodic inhibitors, except $p$-anisidine. The polarization curve of $p$-anisidine showed that inhibitor functions as a mixed inhibitor. The values for the Tafel parameters obtained from this plot with and without inhibitors are given in Table 4. The values of corrosion current densities in the presence and absence of inhibitors were obtained from the plot while efficiency ($\eta$%) was calculated using the relation:

$$\eta(\%) = \left[ \frac{i_{corr}(u) - i_{corr}(i)}{i_{corr}(u)} \right] \times 100$$ \hspace{1cm} \text{(8)}$$

**Mechanism**

Generally, aluminium dissolves in acid solutions due to hydrogen evolution type of attack. The reaction-taking place at the micro electrodes of the corrosion cell may be represented as under,
Al → Al^{3+} + 3e^- (anode) ... (9)

H^+ + e^- → H (cathode) ... (10)

followed by the reaction

H + H → H_2 ... (11)

The following secondary reaction can also take place in acid solutions

2M + 2H^+ → H_2 + 2M^+ (anode) ... (12)

O_2 + 4H^+ + 4e^- → 2H_2O (cathode) ... (13)

If only the hydrogen evolution type of attack predominated and no other factors influenced the corrosion process, corrosion by the strong acid should be maximum.

Possibly, the de-localized π-electrons of anisidines facilitated its strong adsorption on the aluminium surface leading to the high corrosion inhibition efficiency. The presence of –OCH_3 group (an electron donating effect) would enhance the electron density by inductive or mesmeric effect.

The presence of an electron releasing group (–OCH_3) in the anisidine compounds, possibly would increase the rate of formation of the anilinium cation in the order: p-anisidine > o-anisidine > m-anisidine. This is consistent with the results obtained in the present study where o- and p-anisidine gave more inhibition than that for m-anisidine. However, the higher value of inhibition efficiency obtained for o- and p-anisidine might be due to the presence of mesomeric (+M) effect, which is absent in m-anisidine. On the other hand, the lower value of inhibition efficiency for o-anisidine than that of p-anisidine might be attributed to the presence of intermolecular hydrogen bonding and steric effect in o-anisidine, which affect its adsorption and consequently its inhibitive capacity.

The pK_a value of p-anisidine (5.29) is higher than o-anisidine (4.49) and m-anisidine (4.20). Generally, higher the pK_a value of aniline compounds greater its basicity and higher the inhibition efficiency

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (mA/cm²)</th>
<th>Tafel slope (mV/decade)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>+βa</td>
<td>-βc</td>
<td>β (mV)</td>
</tr>
<tr>
<td>Blank</td>
<td>-847</td>
<td>2.650</td>
<td>289.2</td>
<td>308.9</td>
</tr>
<tr>
<td>o-Anisidine</td>
<td>-894</td>
<td>0.256</td>
<td>279.4</td>
<td>371.8</td>
</tr>
<tr>
<td>m-Anisidine</td>
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<td>0.442</td>
<td>289.5</td>
<td>223.5</td>
</tr>
<tr>
<td>p-Anisidine</td>
<td>-880</td>
<td>0.173</td>
<td>168.1</td>
<td>508.9</td>
</tr>
</tbody>
</table>

Table 4—Polarization data and inhibition efficiency of anisidines for aluminium in 0.4 M HCl.

Inhibitor concentration: 80 mM Effective specimen area: 0.0932 dm²

NH_2

OCH_3

NH_2

OCH_3

NH_2

OCH_3

p-anisidine > o-anisidine > m-anisidine

pK_a = 5.29 4.49 4.20

+M +M +M
Conclusions
At constant inhibitor concentration, the inhibition efficiency of all inhibitors decreases as the concentration of acid increases. At all concentration of acid, as the inhibitor concentration increases inhibition efficiency increases and corrosion rate decreases. As the temperature increases corrosion rate increases in plain acid. Addition of inhibitors in corrosive media indicates that as the temperature increases corrosion rate increases while inhibition efficiency decreases. In all cases, the value of heat of adsorption ($Q_{ads}$) and the value of free energy of adsorption ($\Delta G_{ads}^0$) are negative. Value of change of enthalpy ($\Delta H_{ads}^0$) and entropy of adsorption ($\Delta S_{ads}^0$) are positive. Mean value of $E_a$ in inhibited acid are higher than the value of $E_a$ in plain acid. In almost all the cases, the inhibition efficiency from Tafel plots agrees well (within ±8%) with the values obtained from weight loss data.

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Reference