Ethanolamines as corrosion inhibitors for zinc in sulphuric acid

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ABSTRACT
The corrosion of zinc in sulphuric acid containing ethanolamines has been studied at different acid concentrations, inhibitor concentrations and temperatures. Corrosion rate increases with increase in acid concentrations. At constant acid concentration, the inhibition efficiency (I.E.) of ethanolamines increases with inhibitor concentration. Similarly at constant inhibitor concentration, the I.E. increases with the increase in acid concentration. At 60 mM inhibitor concentration in 0.1 M sulphuric acid at 301 K for 24 h immersion period, the I.E. decreases in the order: Ethanolamine (91 %) > Diethanolamine (89 %) > Triethanolamine (86 %). As the temperature increases, corrosion rate increases while I.E. decreases. The mode of inhibition action appears to be chemisorptions since the plot of log (θ/1-θ) versus log C gives a straight line suggest that the inhibitors cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm. Galvanostatic polarization curves showed significant anodic polarization.

Keywords: Corrosion, Zinc, Sulphuric acid, Ethanolamines.

INTRODUCTION
The problem of corrosion is of considerable importance 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. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors [1-3]. According to Hackerman et al. [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. Corry et al. [5] and Manning et al. [6] studied on the relative corrosion rate of alloys tested depends on HCl content on the mixture and reported that addition of HNO₃ to HCl again resulted in decrease in corrosion rate.

Sulphuric acid (H₂SO₄) is a strong acid and is used as a cleaner for rust, algae and scale from condensers and cooling tower [7]. Vashi et al. [8-10] studied ethanolamines as corrosion inhibitors for zinc in binary acid mixture (HNO₃ + H₃PO₄) and (HNO₃ + H₂SO₄). A.S. Fouda et al. [11] studied thiophine derivatives as corrosion inhibitors for CS in 0.5 M H₂SO₄ Inhibition study of Caesalpinia Crista on corrosion of mild steel in H₂SO₄ [12]. The present study was undertaken to evaluate various ethanolamines as corrosion inhibitors for zinc in sulphuric acid.
MATERIALS AND METHODS

Materials: Rectangular specimens (5.5 x 2.5 x 0.2 cm) of zinc having an area of 0.3013 dm$^2$ were used for the determination of the corrosion rate. The chemical composition of test specimen contain 99.39% Zn, 0.49% Mn and 0.12% Co. All specimens were cleaned by buffing to obtain a mirror like finish. All chemicals used were of AR grade. The corrosive solution was prepared in double distilled water.

Weight loss measurements: For weight-loss measurement, the zinc coupons were each suspended and completely immersed in 230 mL of various concentrations like 0.1, 0.3 and 0.5 M H$_2$SO$_4$ solution without and with different concentrations of ethanolamines at 301± 1 K for 24 h immersion period. After the test, the specimen was cleaned by using 10% CrO$_3$ acid solution having 0.2% BaCO$_3$ [13]. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier and reweigh. The mean value of corrosion rate was reported in mg dm$^{-2}$ d$^{-1}$ as shown in table 1.

Temperature effect: To study the effect of temperature on corrosion of zinc in 0.1 M sulphuric acid, the specimens were immersed in 230 ml of the corrosive solution and weight loss was determined at solution temperature of 313, 323 and 333 K for an immersion period of 3 h in absence and presence of three ethanolamines at 60 mM concentration. Attention is paid to compensate the evaporation loss of corrosive media. Wesley [14] and ASTM [15] pointed out that thermostatic control to within ± 1 °C usually be considered satisfactory. From the data, % I.E., energy of activation (Ea), heat of adsorption (Q$_{ads}$), Free energy of adsorption ($\Delta$G$_{a}$), Enthalpy of adsorption ($\Delta$H$_{a}$) and Entropy of adsorption ($\Delta$S$_{a}$) were calculated.

Polarization measurements: For polarization study, metal specimens having as area of 1 cm$^2$ were immersed to 230 mL 0.1 M H$_2$SO$_4$ in absence and presence of ethanolamines in the test cell (using CH instruments, Inc., USA) includes the metal specimens as a working electrode, Ag/AgCl electrode as a reference electrode as well as platinum electrode as an auxiliary electrode and allowed to establish a steady-state open circuit potential (OCP) for approximately 70 min. 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 ($i_{corr}$) and the corrosion potential ($E_{corr}$) [16].

Electrochemical impedance spectroscopy (EIS) measurements: EIS measurements were made (using CH instruments, Inc., USA) at corrosion potentials over a frequency range of 1 KHz to 100 KHz by a sine wave with potential perturbation amplitude of 5 mV. The real $Z'$ and imaginary -$Z''$ parts were measured at various frequencies. From the plot of $Z'$ Vs. -$Z''$, the charge transfer resistance ($R_{ct}$), and double layer capacitance ($C_{dl}$) were calculated. Impedance measurements were carried out both in the absence and presence of inhibitor.

Scanning electron microscope (SEM) study: The zinc specimen immersed in 0.1 M H$_2$SO$_4$ (blank) and containing 60 mM of $o$-toluidine, aniline, ethylamine, ethanolamine as inhibitors for a period of one day at 298 K. After exposure, specimen was removed, rinsed with double distilled water, dried and observed in scanning electron microscope to examine the surface morphology. The SEM image of polished zinc specimen was also taken. The surface morphology measurements of zinc specimens were examined using JEOL-5610 LV (made in Japan) computer controlled SEM.
RESULTS AND DISCUSSION

The results were presented in tables 1 to 4 and in figures 1 to 10. To assess the inhibition effect of corrosion of zinc in sulphuric acid, ethanolamines were added as inhibitors. I.E. has been calculated as follows:

\[
\text{I.E.} \, (\%) = \frac{W_u – W_i}{W_u} \times 100 \tag{1}
\]

Where, \(W_u\) is the weight loss of metal in uninhibited acid and \(W_i\) is the weight loss of metal in inhibited acid.

**Table 1**: Effect of \(\text{H}_2\text{SO}_4\) concentration on corrosion rate (CR) and inhibitor efficiency (I.E.) on zinc metal having different concentration of different amines

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Inhibitor concentration (mM)</th>
<th>Acid concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 M</td>
<td>0.3 M</td>
</tr>
<tr>
<td></td>
<td>CR mg dm(^{-2})d(^{-1})</td>
<td>I. E. %</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>2880.84</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>30</td>
<td>355.59</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>40</td>
<td>105.93</td>
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<tr>
<td>Ethanolamine</td>
<td>50</td>
<td>102.92</td>
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<td>Ethanolamine</td>
<td>60</td>
<td>93.09</td>
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<tr>
<td>Diethanolamine</td>
<td>30</td>
<td>377.43</td>
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<td>40</td>
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<tr>
<td>Diethanolamine</td>
<td>50</td>
<td>121.46</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>60</td>
<td>112.66</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>30</td>
<td>406.32</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>40</td>
<td>159.25</td>
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<tr>
<td>Triethanolamine</td>
<td>50</td>
<td>152.11</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>60</td>
<td>141.13</td>
</tr>
</tbody>
</table>

Energy of activation (\(E_a\)) has been calculated from the slope of log \(\rho\) versus 1/T (\(\rho = \text{corrosion rate}, \ T = \text{absolute temperature}\)) (Fig. 1) and also with the help of the Arrhenius equation [17].

\[
\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \tag{2}
\]

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

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The value of heat of adsorption (Q_{ads}) was calculated using the following equation [18].

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

Where, \( \theta_1 \) and \( \theta_2 \) \([\theta = (W_u - W_i)/W_i]\) are the fractions of the metal surface covered by the inhibitor at temperature \( T_1 \) and \( T_2 \) respectively.

Table 2: Effect of temperature on Corrosion rate (CR), Energy of activation (E_a) and Heat of adsorption (Q_{ads}) for zinc in 0.1 M H_2SO_4 in absence and presence of inhibitors for an immersion period of 3 h.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Inhibitor Conc. (mM)</th>
<th>Temperature (K)</th>
<th>Mean E_a (kJ mol(^{-1}))</th>
<th>‘Ea’ from Arrhenius Plot</th>
<th>Heat of adsorption, Q_{ads} (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>313</td>
<td>10594.08</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Ethanolamine</td>
<td>30</td>
<td>57.39</td>
<td>4513.76</td>
<td>21.79</td>
<td>14.25</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>68.17</td>
<td>3372.00</td>
<td>26.83</td>
<td>26.57</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>75.43</td>
<td>2602.00</td>
<td>26.52</td>
<td>26.31</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>81.95</td>
<td>1911.68</td>
<td>28.15</td>
<td>27.89</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>30</td>
<td>53.89</td>
<td>4832.32</td>
<td>24.95</td>
<td>24.73</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>64.41</td>
<td>4009.28</td>
<td>23.57</td>
<td>23.36</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>74.43</td>
<td>2708.24</td>
<td>30.23</td>
<td>29.93</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>81.20</td>
<td>1991.36</td>
<td>30.63</td>
<td>30.27</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>30</td>
<td>49.62</td>
<td>5336.80</td>
<td>24.49</td>
<td>24.73</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>62.15</td>
<td>4009.28</td>
<td>23.36</td>
<td>23.36</td>
</tr>
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<tr>
<td></td>
<td>60</td>
<td>81.20</td>
<td>1991.36</td>
<td>30.27</td>
<td>30.27</td>
</tr>
</tbody>
</table>

Fig. 2: Arrhenius plots for corrosion of zinc in 0.1 M H_2SO_4 in absence and presence of 60 mM inhibitor concentration.
The values of the free energy of adsorption ($\Delta G_a$) were calculated with the help of the following equation [18].

$$\log C = \log \left( \frac{\theta}{1 - \theta} \right) - \log B \quad \ldots \ldots (4)$$

Where, $\log B = -1.74 - \left( \frac{\Delta G_a}{2.303 \times 10^3 RT} \right)$ and $C$ is the inhibitor concentration. The enthalpy of adsorption ($\Delta H_a$) [19] and entropy of adsorption [20] ($\Delta S_a$) were calculated using the equation.

$$\Delta H_a^0 = \frac{E_a}{T} \quad \ldots \ldots (5)$$

$$\Delta S_a^0 = \frac{\Delta H - \Delta G}{T} \quad \ldots \ldots (6)$$

Inhibitor efficiency (I.E.) from $i_{corr}$ were calculated using following equation.

$$\text{I.E.} (\%) = \frac{i_{corr \ (uninh)} - i_{corr \ (inh)}}{i_{corr \ (uninh)}} \times 100 \quad \ldots \ldots (7)$$

Fig 3: Polarization curve for corrosion of zinc in 0.1 M H$_2$SO$_4$ in absence of inhibitor

Fig 4: Polarization curve for corrosion of zinc in 0.1 M H$_2$SO$_4$ containing 60 mM ethanolamine
Table 3: Polarization data and inhibition efficiency (IE %) of 60 mM ethanolamines for zinc in 0.1 M H₂SO₄.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{corr}$ (V)</th>
<th>$I_{corr}$ (µA/cm²)</th>
<th>Tafel slope (mV/decade)</th>
<th>B (V)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta_a$</td>
<td>$-\beta_c$</td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>-1.094</td>
<td>2.232</td>
<td>0.4133</td>
<td>0.2191</td>
<td>0.0622</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>-1.056</td>
<td>0.1617</td>
<td>0.1148</td>
<td>0.1630</td>
<td>0.0295</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>-1.057</td>
<td>0.1648</td>
<td>0.1248</td>
<td>0.1657</td>
<td>0.0309</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>-1.050</td>
<td>0.1869</td>
<td>0.1104</td>
<td>0.1728</td>
<td>0.0293</td>
</tr>
</tbody>
</table>

$\beta_a$ = Anodic Tafel constant, $\beta_c$ = Cathodic Tafel constant.
CD = Corrosion current density from interception of anodic and cathodic lines.

The charge transfer resistance ($R_{ct}$) values were calculated from the difference in impedance at lower and higher frequencies. To obtain the double layer capacitance ($C_{dl}$), the frequency at which the imaginary component of the impedance maximum was found as presented in the following equation [21].

$$C_{dl} = \frac{1}{2 \pi f R_{ct}}$$  

Where, $f$ is the frequency at the maximum height of the semicircle on the imaginary axis and $R_{ct}$ is the charge transfer resistance [22]. I.E. from $C_{dl}$ values were calculated using following equation.

$$I.E. (%) = \frac{C_{dl} \text{ (uninh) } - C_{dl} \text{ (inh) }}{C_{dl} \text{ (uninh) }} \times 100$$  

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Fig 7: Nyquist plot for corrosion of zinc in 0.1 M H$_2$SO$_4$ without inhibitor

Fig 8: Nyquist plot for corrosion of zinc in 0.1 M H$_2$SO$_4$ containing 60 mM ethanolamine

Fig 9: Nyquist plot for corrosion of zinc in 0.1 M H$_2$SO$_4$ containing 60 mM diethanolamine

Fig 10: Nyquist plot for corrosion of zinc in 0.1 M H$_2$SO$_4$ containing 60 mM triethanolamine.

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Table 4: EIS parameters for the corrosion of zinc in 0.1 M H₂SO₄ in absence and presence of 60 mM ethanolamines

<table>
<thead>
<tr>
<th>System</th>
<th>Rₛ (Ω cm²)</th>
<th>Cₛ (μF cm²)</th>
<th>IE (%) Calculated from EIS method</th>
<th>Weight loss method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>49.5</td>
<td>151.84</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>340.0</td>
<td>3.12</td>
<td>97.94</td>
<td>91.01</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>373.0</td>
<td>2.84</td>
<td>98.12</td>
<td>89.12</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>270.0</td>
<td>5.36</td>
<td>96.94</td>
<td>86.37</td>
</tr>
</tbody>
</table>

Figure 11: SEM micrograph of zinc (a) polished zinc plate (1000X), immersion in 0.1 M zinc in absence of inhibitor (1000X), (c) immersion in 0.1 M zinc in presence of 60mM ethanolamine inhibitor after 24h (1000X).

Corrosion by sulphuric acid: The corrosion rate increases with the increase in acid concentration. The corrosion rate was 1035.50, 2880.84 and 6179.88 mg dm⁻² d⁻¹ correspond to 0.1, 0.3 and 0.5 M H₂SO₄ concentrations respectively for a period of 24 h at 301 ± 1 K as shown in table-1.

Effect of inhibitor concentration: At constant acid concentration, the I.E. of the ethanolamines increases with the inhibitor concentration, e.g. In 0.1 M H₂SO₄ the I.E. for ethanolamine were found to be 65.66, 89.77, 90.06 and 91.01%, for diethanolamine I.E. were 63.55, 85.42, 88.27 and 89.12% and for triethanolamine I.E. were 61.05, 84.62, 85.31 and 86.37% correspond to 30, 40, 50 and 60 mM inhibitor concentration respectively (Table-1).

Effect of acid concentration: At constant inhibitor concentration, the I.E. increases with the increase in acid concentration. At 60 mM inhibitor concentration, the I.E. of ethanolamine were 91.01, 94.08 and 95.38 %, for diethanolamine it was 89.12, 92.98 and 94.02% and for triethanolamine it were 86.37, 91.52 and 93.67% correspond to 0.1, 0.3 and 0.5 M acid concentration respectively (Table-1).

Effect of temperature: To determine the effect of temperature on corrosion, corrosion loss was measured in 0.1 M sulphuric acid containing 30, 40, 50 and 60 mM inhibitor concentration at solution temperature of 313, 323 and 333 K for an immersion period for 3 h. As the temperature is increases, corrosion loss
increases while percentage of I.E. decreases (Table-2). Corrosion loss increases with temperature may be due to the desorption of the adsorbed molecules inhibitor and/ or aggressive at higher temperature and thus exposing the fresh metal surface to further attack [23], which results in intensification of the kinetic of electrochemical reaction [24] and thus explains the higher corrosion rate at elevated temperature. The addition of ethanolamines in corrosive media indicates that as the temperature increases I.E. decreases, e.g. in 0.1 M H₂SO₄ at 60 mM inhibitor concentration, the I.E. for ethanolamine was 81.95, 78.15 and 75.09% at 313, 323 and 333 K respectively.

**Energy of activation (Eₐ):** The mean “Eₐ” value calculated from equation (2) for zinc in 0.1 M H₂SO₄ was 14.25 kJ mol⁻¹. A comparison of the values of the Eₐ for the corrosion process in inhibited (in the range 21.79 to 35.66 kJ mol⁻¹) which indicates that the “Eₐ” values were higher in inhibited than in uninhibited acid (Table-2). The higher values of mean Eₐ, indicates physical adsorption of the inhibitors on metal surface [25]. The value of Eₐ calculated from the slope of Arrhenius plot (Fig. 1) and using equation 2 were almost similar.

**Heat of adsorption (Q_ads):** From table 2 it was evident in all cases Q_ads values were negative and ranging from -13.07 kJ mol⁻¹ to -34.66 kJ mol⁻¹. As the temperature increases values of Q_ads decreases (become more negative). The negative Q_ads values shows that the adsorption and hence the I.E. decreases with rise in temperature [26].

**Adsorption isotherm:** The graph of log [θ / (1 - θ)] vs. log C for aliphatic amines (ethanalamine, diethanalamine and triethanolamine) in 0.1 M H₂SO₄ was depicted in figure 2. A straight line was obtained proving the fact that the adsorption of these three inhibitors on the zinc surface obeys the Langmuir adsorption isotherm.

**Free energy of adsorption (ΔG°ₐ):** The values of mean ΔG°ₐ were calculated. In all cases mean ΔG°ₐ values were negative and lie in the range of -19.45 (30 mM triethanolamine) to -21.78 (60 mM ethanolamine). The negatives values of (ΔG°ₐ) indicated the spontaneous adsorption of the inhibitor. This is usually characteristic of strong interaction with metal surface. It was found that the ΔG°ₐ values more positive than -40 kJ mol⁻¹, indicating that inhibitor is physically adsorbed on the metal surface [19].

**Enthalpy of adsorption (ΔH°_ads):** The enthalpy of adsorption (ΔH°_ads) were positive as 18.68 kJ mol⁻¹ (for 30 mM ethanolamine) to 37.61 kJ mol⁻¹ (for 60 mM triethanolamine) indicating the endothermic nature of the reaction [19] suggesting that higher temperature favors the corrosion process.

**Entropy of adsorption (ΔS°_ads):** The entropy (ΔS°_ads) values were positive as 0.12 kJ mol⁻¹ (for 30 mM ethanolamine) to 0.18 kJ mol⁻¹ (for 60 mM triethanolamine) confirming that the corrosion process is entropically favorable [20].

**Potentiodynamic Polarization measurements:** Potentiodynamic polarization curve for zinc in 0.1 M H₂SO₄ in absence and presence of 60 mM ethanolamines were shown in fig.-3 to fig.-6. Associated electrochemical parameters such as corrosion potential (E_corr), corrosion current density (i_corr) anodic Tafel slope (βₐ), cathodic Tafel slope (βₐ) and percentage inhibition efficiency (I.E.) were given in Table 3. The curves show polarization of both, the cathodes as well as anodes. (Fig. 3-6) I.E. calculated from corrosion current obtained by the extrapolation of the cathodic and anodic Tafel lines were 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.

**Electrochemical impedance spectroscopy (EIS) measurements:** Corrosion of zinc in 0.1 M H₂SO₄ in presence of ethanolamines was investigated by EIS measurement at room temperature. Nyquist plots for zinc obtain in absence and presence of ethanolamines were shown in (Fig. 7-10) and table-4. The addition
of inhibitor increase $R_{ct}$ value while $C_{dl}$ decrease. This decrease in $C_{dl}$ value was due to the adsorption of inhibitor on metal surface. The results suggest that the inhibitor acts by the formation of a protective layer on the surface, which modifies the metal/solution interface. It was observed that from that the impedance diagram was almost semicircular in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion [27]. The semicircle nature of the plots indicates that the corrosion of zinc is mainly controlled by charge transfer process.

**Scanning electron microscope (SEM) measurement:** To understand the surface conditions of the metal specimen in the absence and presence of inhibitors SEM images are taken. The morphology of the polished zinc plate is very smooth and shows no corrosion (a) while zinc specimens dipped in a 0.1 M sulphuric acid in the absence of inhibitor (b) is very rough and the surface was damaged due to metal dissolution. However, the presence of 60 mM of ethanolamine inhibitors suppresses the rate of corrosion and surface damaged has been diminished considerably (c) as compared to the blank solution (b) which suggest the formation of a protective inhibitor film at the zinc surface. As the inhibitor gets adsorbed by physisorption and binds on the metal surface, it shows less abrasion as compared to uninhibited conditions.

**Mechanism of corrosion and inhibition:** Sulphuric acid acts as strong acid. The probable chemical reaction taking place in sulphuric acid is as under. It undergoes hydrolysis in aqueous solution.

$$2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{O}^+ + 2\text{HSO}_4^- \quad \ldots (10)$$

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

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \text{ (anodic reaction)} \quad \ldots (11)$$

Reduction reaction is indicated by a decrease in valence or the consumption of electrons.

$$2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H} \text{ (Cathodic reaction)} \quad \ldots (12)$$

$\text{H}_2$ gas is liberated by any of the two following reactions:

$$\text{H} + \text{H} = \text{H}_2 \uparrow \quad \ldots (13)$$

or $$\text{H} + \text{H}^+ + \text{e}^- = \text{H}_2 \uparrow \quad \ldots (14)$$

or $$\text{H} + \text{H}_3\text{O}^+ + \text{e}^- = \text{H}_2 \uparrow + \text{H}_2\text{O} \quad \ldots (15)$$

Corrosive attack of sulphuric acid on zinc may be mainly due to the formation of $\text{HSO}_4^-$ during the ionization of acid. However, inhibitors prevent the auto-catalytic cycle of the formation of $\text{HSO}_4^-$ which results into inhibitor of the corrosion of zinc in sulfuric acid.

In sulphuric acid generally at all inhibitor concentration the order of I.E. of these three amines was as follows: ethanolamine $>$ diethanolamine $>$ triethanolamine.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>pKa</th>
<th>l.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanolamine</td>
<td>9.50</td>
<td>3</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>8.88</td>
<td>5</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>7.77</td>
<td>7</td>
</tr>
</tbody>
</table>

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Among ethanolamines the pka value decreases in the following order: 9.50 (ethanolamine) > 8.88 (diethanolamine) > 7.77 (triethanolamine). The result shows that higher the pka value higher will be the basicity and higher the I.E.

Lone pair is increases in the following order: 3 (ethanolamine) < 5 (diethanolamine) < 7 (triethanolamine). This indicates that as the lone pair increases corrosion rate also increases and I.E. decreases.

As the number of ethanol groups increases on nitrogen atom, it increases crowding around nitrogen atom. This crowding result in strain is less in ethanolamine and maximum in triethanolamine. Due to this, the stability of molecule is high in ethanolamine than triethanolamine and so basicity is also reduced. Because of this effect ethanolamine gave higher inhibition than di and triethanolamine in H<sub>2</sub>SO<sub>4</sub>.

The results are in agreement with the work of Vashi and Champaneri [28], Vashi and Diksha Naik [29], Vashi and Bhajiwala [30], and Vashi et al. [9] and found percentage inhibition in the order: ethanolamine > diethanolamine > triethanolamine. The better inhibiting characteristic of secondary amine than tertiary amine can be explained by steric hindrance in tertiary amines, which may have influence as the electron density and on the base strength [31]. The order can be explained on the basis of the influence of electron withdrawing ability of OH group in alkanol group and the overcrowding on the nitrogen atom [32].

**CONCLUSIONS**

- As the acid concentration increase the corrosion rate increases.
- At constant inhibitor concentration, the I.E. of ethanolamines increases as the concentration of acid increases. At all concentration of acid, as the inhibitor concentration increases I.E. increases and corrosion rate decreases.
- At 60 mM inhibitor concentration and 0.1 M acid concentration ethanolamine shows better I.E. while triethanolamine shows less effective.
- As the temperature increases corrosion rate increases while I.E. decreases.
- In all cases, the value of heat of adsorption (Q_{ad}) and the value of free energy of adsorption (ΔG_a) were negative. Value of change of enthalpy (ΔH) and entropy of adsorption (ΔS) were positive.
- Mean value of ‘Ea’ in inhibited acid were higher than the value of ‘Ea’ in acid only, which shows that chemisorption of the inhibitor molecule.
- log (θ/1-θ) Vs log C (inhibitor concentration) shows straight line, which indicate that the inhibition action appears to be the chemisorption and inhibitors cover both anodic and cathodic region through general adsorption following Langmuir isotherm.
- Results obtained from polarization method and EIS methods were in good agreement with weight loss method.
- Polarization curves shows somewhat less cathodic polarization and greater anodic polarization in presence of inhibitor.
- SEM shows smoother surface of inhibited metal samples than inhibited samples due to the formation of a protective layer on inhibited metal sample.

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REFERENCES


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