N-ETHYL N-HYDROXYETHYL ANILINE (NENHEA) AS CORROSION INHIBITOR FOR MILD STEEL IN 0.5 M SULFURIC ACID

Abstract
The efficiency of N-ethyl N-hydroxyethyl aniline (NENHEA) as corrosion inhibitor for mild steel in 0.5 M sulfuric acid has been investigated electrochemically by potentiodynamic and potentiostatic techniques, and surface morphology analysis by scanning electron microscopy. The results showed that the efficiency of NENHEA increases with the concentration and decreases with temperature. Corrosion potential indicate that this is an inhibitor of mixed type, although it is predominantly cathodic inhibitor. The adsorption of NENHEA on mild steel obeys Langmuir-Freundlich isotherm.

Keywords: Corrosion Inhibitor, Mild Steel, SEM, Langmuir-Freundlich Isotherm

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Resumo
A eficiência do inibidor de corrosão N-ethyl N-hidroxietil anilina (NENHEA) para o aço macio em 0,5M de ácido sulfúrico tem sido estudada por métodos electroquímicos através de técnicas potenciocinâmicas e potenciosstáticas e por análise de superfícies ocorrendo à microscopia electrónica de varrimento. Os resultados demonstram que a eficiência do NENHEA aumenta com a concentração e diminui com a temperatura. Os dados do potencial de corrosão indicam que este inibidor é do tipo misto, embora seja predominantemente do tipo catódico. A adsorção do NENHEA ao aço macio obedece ao modelo de isotérmicas Langmuir-Freundlich.

Palavras Chave: Inibidor de Corrosão, Aço Macio, MEV, Isotérmica Langmuir-Freundlich

1. INTRODUCTION
Corrosion of metals is a major industrial problem that has attracted a lot of investigators in recent years [1-3]. Most of the efficient inhibitors used in industry are organic compounds that contain hetero-atoms (N, S, O) and/or multiple bonds in the molecules through which they are adsorbed onto the metal surface [4]. The existing literature shows that corrosion inhibition is a surface phenomenon which involves the adsorption of the organic compounds on metal surface [5, 6]. It has been observed that inhibition efficiency of organic compounds depends on electronic structure, molecular size, concentration of the molecules, surface morphology of the metal, the type of acid and interaction between metal and compound [7]. Large numbers of organic compounds with N as heteroatom, like amines, anilines, imines, imides have been studied as corrosion inhibitors [8-27]. In the present work, a study has been conducted on N-ethyl N-hydroxyethyl aniline (NENHEA, Molar Mass = 165.23 g mol\(^{-1}\)) as corrosion inhibitor for mild steel in sulphuric acid. This compound has been investigated because it has heteroatoms like N and O [28], electron donating groups like ethyl, hydroxyl and n-electrons. Fig. 1 depicts the structure of the compound.

Fig. 1 - Structure of NENHEA

2. METHODOLOGIES
The corrosion of mild steel in the presence and absence of NENHEA has been investigated by potentiodynamic polarization, potentiostatic polarization and surface analysis.

2.1 Mild steel specimen
Experiments have been carried out using mild steel samples (C = 0.15%; Mn = 1.02%; Si = 0.025%; P = 0.025% and the remainder iron) with an exposed area of 1 cm\(^2\).

2.2 Potentiodynamic polarization studies
Cathodic and anodic polarization studies have been performed on mild steel in 0.5 M H\(_2\)SO\(_4\) in the presence of 10\(^{-1}\), 10\(^{-3}\), 10\(^{-5}\) and 10\(^{-7}\) M of NENHEA at 298, 308, 318 and 328 K. Three electrodes system was used, calomel electrode as reference electrode, platinum electrode as counter electrode and metal electrode as working electrode. The working electrode and reference electrode was immersed in a test solution for 4 hours until a steady state open circuit potential (OCP) was obtained. The current was passed to cell through the counter electrode and the cathodic polarization curve was obtained. Then after the regeneration of OCP, anodic polarization was obtained.

2.3 Potentiostatic polarization studies
Three electrodes system was used for potentiostatic polarization studies and the potential was applied through the cell at different values and the corresponding current values were noted. Polarization was carried out on mild steel in 0.5 M H\(_2\)SO\(_4\) in the presence of 10\(^{-1}\), 10\(^{-3}\), 10\(^{-5}\) and 10\(^{-7}\) M NENHEA at 298 K.

2.4 Scanning electron microscopy (SEM):
Polished cube of mild steel (1x1x1 cm) was taken and washed with acetone and dried in dessicator. Mild steel coupons were dipped in 0.5 M H\(_2\)SO\(_4\) in the presence of 10\(^{-1}\), 10\(^{-3}\) and 10\(^{-5}\) M of NENHEA solution for 24 hours. They were then removed carefully without touching the surface, dried in a dessicator for 24 hours and then subjected to JEOL JSM 840 scanning electron microscope for SEM studies.

3. RESULTS
3.1 Potentiodynamic polarization studies
Figs. 2 a) to 2d) show the cathodic and anodic potentiodynamic curves obtained in 0.5 M H\(_2\)SO\(_4\) for different concentration of NENHEA at several temperatures.

The corrosion current densities (i\(_{corr}\)) were obtained by extrapolation of cathodic and anodic curves. Inhibition efficiency (%) was calculated using Eqn. 1.

VOLTAR AO INÍCIO
Where $i_{in}$ and $i_o$ are, respectively, the corrosion current densities in inhibited and uninhibited solution. The values of various electrochemical parameters taken from the results such as the corrosion potential ($E_{corr}$), cathodic Tafel slope ($b_c$), anodic Tafel slope ($b_a$), $i_{corr}$ and $I%$ are summarized in Table 1.

**Table 1 - Electrochemical parameters of mild steel in 0.5 M H$_2$SO$_4$ containing NENHEA.**

<table>
<thead>
<tr>
<th>Temp./K</th>
<th>Conc./M</th>
<th>$E_{corr}$/mV</th>
<th>$b_c$/mV dec$^{-1}$</th>
<th>$b_a$/mV dec$^{-1}$</th>
<th>$i_{corr}$/10$^{-3}$ mA cm$^{-2}$</th>
<th>$I%$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>10$^{-1}$</td>
<td>492.9</td>
<td>121.4</td>
<td>93.6</td>
<td>0.336</td>
<td>87.7</td>
<td>0.877</td>
</tr>
<tr>
<td></td>
<td>10$^{-3}$</td>
<td>486.7</td>
<td>133.3</td>
<td>60.0</td>
<td>0.357</td>
<td>84.3</td>
<td>0.842</td>
</tr>
<tr>
<td></td>
<td>10$^{-5}$</td>
<td>453.3</td>
<td>133.3</td>
<td>46.7</td>
<td>0.362</td>
<td>83.4</td>
<td>0.834</td>
</tr>
<tr>
<td></td>
<td>10$^{-7}$</td>
<td>506.7</td>
<td>106.7</td>
<td>73.3</td>
<td>0.389</td>
<td>76.6</td>
<td>0.766</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>465.8</td>
<td>106.7</td>
<td>120.0</td>
<td>0.489</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>308</td>
<td>10$^{-1}$</td>
<td>476.9</td>
<td>153.9</td>
<td>53.9</td>
<td>0.347</td>
<td>85.8</td>
<td>0.858</td>
</tr>
<tr>
<td></td>
<td>10$^{-3}$</td>
<td>486.7</td>
<td>123.3</td>
<td>80.0</td>
<td>0.398</td>
<td>74.9</td>
<td>0.749</td>
</tr>
<tr>
<td></td>
<td>10$^{-5}$</td>
<td>493.7</td>
<td>106.2</td>
<td>75.0</td>
<td>0.402</td>
<td>73.4</td>
<td>0.734</td>
</tr>
<tr>
<td></td>
<td>10$^{-7}$</td>
<td>482.4</td>
<td>105.9</td>
<td>78.5</td>
<td>0.419</td>
<td>66.5</td>
<td>0.665</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>471.0</td>
<td>93.8</td>
<td>58.1</td>
<td>0.491</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>318</td>
<td>10$^{-1}$</td>
<td>466.7</td>
<td>106.7</td>
<td>53.3</td>
<td>0.394</td>
<td>85</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>10$^{-3}$</td>
<td>479.4</td>
<td>88.2</td>
<td>58.8</td>
<td>0.435</td>
<td>73.4</td>
<td>0.734</td>
</tr>
<tr>
<td></td>
<td>10$^{-5}$</td>
<td>488.2</td>
<td>94.2</td>
<td>53.0</td>
<td>0.437</td>
<td>72.7</td>
<td>0.727</td>
</tr>
<tr>
<td></td>
<td>10$^{-7}$</td>
<td>500.0</td>
<td>70.4</td>
<td>58.8</td>
<td>0.479</td>
<td>48.5</td>
<td>0.485</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>478.6</td>
<td>42.9</td>
<td>28.6</td>
<td>0.519</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>328</td>
<td>10$^{-1}$</td>
<td>464.7</td>
<td>117.6</td>
<td>52.9</td>
<td>0.451</td>
<td>78.9</td>
<td>0.789</td>
</tr>
<tr>
<td></td>
<td>10$^{-3}$</td>
<td>482.4</td>
<td>82.4</td>
<td>70.6</td>
<td>0.470</td>
<td>71.8</td>
<td>0.406</td>
</tr>
<tr>
<td></td>
<td>10$^{-5}$</td>
<td>458.8</td>
<td>153.2</td>
<td>47.1</td>
<td>0.495</td>
<td>57.8</td>
<td>0.088</td>
</tr>
<tr>
<td></td>
<td>10$^{-7}$</td>
<td>485.0</td>
<td>80.0</td>
<td>55.0</td>
<td>0.509</td>
<td>46.9</td>
<td>0.054</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>500.0</td>
<td>100.0</td>
<td>100.0</td>
<td>0.544</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2 Adsorption isotherm

The surface coverage ($\theta$) is calculated using the equation,

$$\theta = \left(\frac{I%}{100}\right)$$

The adsorption behavior of the NENHEA on the metal surface was studied by fitting the data to various isotherms. Fig. 3 shows a straight line obtained on plotting $\log(\theta/(1-\theta))$ vs. $\log c$ (with a slope which is not equal to unity) suggesting that the adsorption of NENHEA on mild steel in H$_2$SO$_4$ follows Langmuir-Freundlich isotherm (correlation coefficient $R^2=0.9231$).

**Fig. 2 - Potentiodynamic polarization curves for mild steel in 0.5 M H$_2$SO$_4$ with different concentrations of NENHEA at (a) 298, (b) 308, (c) 318 and (d) 328 K.**

**Fig. 3 - Langmuir-Freundlich adsorption isotherms at different temperatures.**

Langmuir-Freundlich adsorption isotherm is given by Eqn. 3

$$\left(\frac{\theta}{1-\theta}\right) = K'c^x$$

Where $K$ is equilibrium constant = $K'x$, $c$ is concentration, $\theta$ is surface coverage and $x$ is number of inhibitor occupy in one active site. Using Eqn. 3, equilibrium constant, $K$ is calculated at different temperatures and is given in Table 2.
The free energy of adsorption at different temperatures is also calculated from the values of K using Eqn. 4

$$\Delta G_{\text{ads}}^0 = -RT \ln (55.5K)$$

(4)

Table 2 – Equilibrium Constant and standard free energy for the adsorption of mild steel in 0.5 M H$_2$SO$_4$ in the presence of NENHEA.

<table>
<thead>
<tr>
<th>Temp./ K</th>
<th>Equilibrium Constant</th>
<th>$\Delta G_{\text{ads}}^0 / $kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>2.5 X 10$^{17}$</td>
<td>-109.24</td>
</tr>
<tr>
<td>308</td>
<td>5.2 X 10$^{19}$</td>
<td>-73.50</td>
</tr>
<tr>
<td>318</td>
<td>2.4 X 10$^{7}$</td>
<td>-55.58</td>
</tr>
<tr>
<td>328</td>
<td>2.0 X 10$^{6}$</td>
<td>-50.53</td>
</tr>
</tbody>
</table>

Eqn. 4 can also be written as

$$\Delta G_{\text{ads}}^0 = -RT \ln (55.5K) = \Delta H_{\text{ads}}^0 - T \Delta S_{\text{ads}}^0$$

(5)

Rearrangement of Eqn. 5 shows that the plot of log K vs. 1/T should be a straight line. $\Delta H_{\text{ads}}^0$ and $\Delta S_{\text{ads}}^0$ can be calculated from the slope and intercept respectively. Fig. 4 shows the plot of log K vs. 1/T.

The values of $\Delta H_{\text{ads}}^0$ and $\Delta S_{\text{ads}}^0$ are found to be -701.55 kJ mol$^{-1}$ and -2.01 kJ K$^{-1}$ mol$^{-1}$ respectively.

3.3 Effect of temperature

Eqn. 6 is used for calculating the energy of activation for the corrosion process.

$$k = A e^{-E_a/RT} = i_{\text{corr}}$$

(6)

Where A is Arrhenius constant, $E_a$ is activation energy, $i_{\text{corr}}$ is the corrosion current. Fig. 5 shows the plot of log $i_{\text{corr}}$ vs. 1/T and Table 3 gives the values of activation energy at different concentrations of NENHEA.

The values of $\Delta H_{\text{ads}}^0$ and $\Delta S_{\text{ads}}^0$ are found to be -701.55 kJ mol$^{-1}$ and -2.01 kJ K$^{-1}$ mol$^{-1}$ respectively.

3.4 Potentiostatic polarization studies

Passivity affects the mechanism of corrosion process because it produces a protective film that acts as a barrier to attack on the metal surface by the acidic environment. The effects of these additives have been studied in terms of electrochemical parameters, i.e., critical current ($i_c$), primary passivation current ($i_{pp}$), primary passivation potential ($E_{pp}$) are shown in Fig. 6 and the corresponding data are given in Table 4.

Fig. 4 - Plot of log K vs. 1/T

Fig. 5 - Plot of log $i_{\text{corr}}$ vs. 1/T for various concentrations of NENHEA.

Fig. 6 - Potentiostatic polarization curve for mild steel in 0.5 M H$_2$SO$_4$ at various concentrations of NENHEA.

Table 3 - Energy of activation of mild steel in 0.5 M H$_2$SO$_4$ in the presence of NENHEA.

<table>
<thead>
<tr>
<th>Conc. / mol L$^{-1}$</th>
<th>$E_a$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>27.96</td>
</tr>
<tr>
<td>10$^{-1}$</td>
<td>42.41</td>
</tr>
<tr>
<td>10$^{-3}$</td>
<td>43.08</td>
</tr>
<tr>
<td>10$^{-5}$</td>
<td>51.43</td>
</tr>
<tr>
<td>10$^{-7}$</td>
<td>51.93</td>
</tr>
</tbody>
</table>

Table 4 - Corrosion parameters of mild steel in 0.5 M H$_2$SO$_4$ in the presence of NENHEA.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. / mol L$^{-1}$</th>
<th>$E_{pp}$ range / mV</th>
<th>$i_{pp}$ / mA cm$^{-2}$</th>
<th>$i_c$ / mA cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NENHEA</td>
<td>10$^{-1}$</td>
<td>1400.0 - 360.0</td>
<td>1.23</td>
<td>138.08</td>
</tr>
<tr>
<td></td>
<td>10$^{-3}$</td>
<td>1150.0 - 400.0</td>
<td>3.16</td>
<td>169.82</td>
</tr>
<tr>
<td></td>
<td>10$^{-5}$</td>
<td>1000.0 - 300.0</td>
<td>6.31</td>
<td>83.186</td>
</tr>
<tr>
<td></td>
<td>10$^{-7}$</td>
<td>1000.0 - 400.0</td>
<td>7.76</td>
<td>109.65</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>0.5</td>
<td>1000.0 - 600.0</td>
<td>9.55</td>
<td>301.94</td>
</tr>
</tbody>
</table>
Table 4 shows that the passivation in 0.5 M solution of sulphuric acid and 0.1 M NENHEA occurs in the range of potential between 360 and 1400 mV, while to the solution without inhibitor is 600 to 1000 mV. The value of $i_{p}$ decreases from 9.55 mA/cm² for the uninhibited solution to 1.23 mA/cm² for the solution containing 10⁻¹ M concentration of inhibitor, while this change is from 9.55 mA/cm² to 7.76 mA/cm² for the solution containing 10⁻⁷ M concentration of inhibitor. $E_{p}$ increases with the concentration of inhibitor conversely to $i_{p}$ that decreases.

This additive undergoes protonation to a considerable extent in H₂SO₄ [29], therefore the protonated species are not effective towards metal dissolution in active range, but becomes effective in passive range. The already adsorbed species like Fe(oH)ads may interact with those protonated species forming adsorbed layer on the surface and the complex of the type:

$$\text{Fe}_{6}[\text{Fe(OH)}_{3}]\text{-oxidelayer} + \text{InH}^{+} \rightarrow \text{Fe}_{6}[\text{Fe-In-(OH)}_{3}]$$

Passivity may be due to the formation of [M-In-oH]ads or [M-oH-In]ads or [M-In-X]ads, where Xs are other anions present in the solution that may control the process. The irregular trends in Tafel slope values seem to confirm this hypothesis.

On comparing the surfaces of mild steel it turns out that the extent of corrosion decreases with increasing concentration of the inhibitor, in agreement with electrochemical results.

In synthesis we can say that NENHEA protects the mild steel surface by:
- Neutralization of acid and making the medium less corrosive.
- Adsorption as well as by donating electrons from heteroatom like N and O.
- Protonated species adsorbed on the metal surface that reduce the hydrogen release.

**CONCLUSIONS**

N-Ethyl N-Hydroxyethyl aniline was used to protect the mild steel in 0.5 M sulfuric acid. The corrosion inhibition and adsorption characteristics have been studied by potentiodynamic and potentiostatic polarization at different concentrations and temperatures.
It can be concluded that:
1. NENHEA protects the mild steel in H₂SO₄ by getting adsorbed on the metal surface.
2. The corrosion inhibition efficiency increases with the concentration of NENHEA.
3. The inhibition efficiency decreases with temperature.
4. It is a mixed type of inhibitor but acts predominantly as cathodic inhibitor.
5. The adsorption of NENHEA on a mild steel surface obeys Langmuir-Freundlich isotherm.
6. NENHEA physically adsors on the mild steel surface in sulfuric acid since ΔG°ₚ≤80 kJ/mol.
7. The values of Eₐ increases with the concentration of inhibitor.
8. SEM results agree well with electrochemical results.

REFERENCES