A Thesis
Submitted to The Department of Materials Engineering- University of Technology
in APartial Fulfillment of The Requirements for The Degree of Master of Science
in Materials Engineering

By

Rana Sahib Noor

(B.Sc. in Materials Engineering 2002)

Supervised by

Asst. Prof. Dr. Mohammed Hliyil Hafiz  Asst. Prof. Dr. Rana Afif Majed

November 2013 A.DMoharam1435 A.H
Abstract

This thesis includes study of corrosion inhibition of carbon steel (which is used in Al-Durra refinery at vacuum distillation unit as body of separating vessels) in sour medium which contains H₂S and ammonium using electrochemical technique by Potentiostat/Galvanostat instrument at heat temperature of 75°C. Four sour media have been obtained from light and heavy naphtha units and then selected the medium which has the highest electrical conductivity and the most contents of H₂S and NH₄⁺.

Four amines were selected as corrosion inhibitors; two liquids aliphatic amines: dibutylamine (DBA) with four concentrations (0.0237, 0.0356, 0.0475 and 0.0593M); and cyclohexylamine (CHA) with four concentrations (0.0349, 0.0523, 0.0698, and 0.0872M), and two solid aromatic amines: diphenylamine (DPA) and phenylenediamine (PDA) with four concentrations of each one of them (1x10⁻⁵, 1x10⁻⁴, 1x10⁻³ and 1x10⁻² M). Corrosion parameters have been measured such as corrosion potentials \( E_{\text{corr}} \) and corrosion current densities \( i_{\text{corr}} \), in addition to cathodic and anodic Tafel slopes \( b_c \& b_a \) by Tafel extrapolation method, corrosion rates also are calculated in mm/y. The data showed that the presence of these amines shifted, in general, corrosion potential toward noble direction and corrosion current density values became lower. The data of Tafel slopes indicate that aliphatic amines behave as mixed inhibitor type, while aromatic amines are anodic inhibitors.

Protection efficiencies \( P\% \) were calculated and the results showed that all selected amines are acting as good inhibitors, and there are best concentration of each amine which gives the best efficiency as follow:

<table>
<thead>
<tr>
<th>Inhibitor Conc.</th>
<th>DBA 0.0237M</th>
<th>CHA 0.0872M</th>
<th>PDA 1x10⁻³M</th>
<th>DPA 1x10⁻²M</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P% )</td>
<td>92.28</td>
<td>&gt; 90.78</td>
<td>&gt; 90.45</td>
<td>&gt; 85.81</td>
</tr>
</tbody>
</table>

Cyclic polarization curves have been recorded and their results were
agreement with the results of linear polarization obtained from galvanodynamic tests for the current in the range of -15 to +15 mA. From cyclic polarization curves it can be seen the decreasing in hysteresis loop compared with the test in the absence of inhibitors, or disappear of hysteresis loop which indicates the decreasing of chances of the occurrence of pitting and crevice corrosion.

FTIR spectra has been used to explain the role of inhibitive action of selected amines, where indicates the decreasing in N—H stretching band of amine in the film formed on the steel surface due to adsorption of amine on the metallic surface and suggests that nitrogen of amine group is coordinated with Fe$^{2+}$ on the anodic sites of the metal surface to form Fe$^{2+}$—N—complex, in addition to the reduction of broad band which appears in the absence of inhibitor due to H—bonded between the iron ions and the water molecules from medium. This bonding may be due to solvation of metallic ions at electrical double layer.

Optical and scanning electron microscopes support the results of electrochemical measurements and FTIR spectra. Flakes which show corrosion products are observed in the micrographs. The micrographs revealed that the surface has been strongly damaged owing to corrosion in absence of the inhibitor, but in the presence of the inhibitor, the damage on the surface seemed to be smaller. This is attributed to the formation of a good protective film on the low carbon steel surface.

The selected amines obeyed Langmiur isotherm type. The negative values of Gibbs free energy $\Delta G^o_{ads}$ indicate the spontaneous adsorption of four inhibitors. Large values of $K_{ads}$ imply more efficient adsorption and hence better inhibition efficiency. The negative sign of the change of enthalpy $\Delta H^o_{ads}$ in sour medium indicates that the adsorption of inhibitor molecules is an exothermic process. The
negative values of the change of entropy $\Delta S_{\text{ads}}$ are indicating that amines retained the mobility of metal ions and reducing the dissolution of carbon steel.

**Keywords** : Sour corrosion, H$_2$S corrosion, corrosion inhibition, carbon steel, sour medium, amines, dibutylamine, cyclohexylamine, diphenylamine, phenylenediamine, electrochemical test, FTIR spectra, SEM