INHIBITING EFFECTS OF ORGANIC INHIBITOR ON CORROSION OF STEEL IN 3.5% BRINE SOLUTION

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The experiment for API grade steel has been carried out by using weight loss measurement technique. All the experiments were carried out in an autoclave at varying temperature and a fixed partial pressure of carbon dioxide. The different concentration of imidazoline as organic inhibitor has been added in the solution to know the inhibition effect on the metal surface. The results indicated that addition of 40 ppm of inhibitor showed the higher efficiency due to the formation of more adhered and protective film over the metal surface. The exposed samples were characterized by using various techniques such as x-ray photoelectron spectroscopy and scanning electron microscopy.

Keywords: Imidazoline inhibitor, Brine solution, Autoclave, SEM, FTIR

INTRODUCTION

Inhibitors are the chemical substances that react with a metallic surface exposed in the corrosive environment. Usually, inhibitors are used to protect the metallic surface by forming a corrosion film. These inhibitors are often work by adsorbing themselves on the metallic surface, and thus preventing the surface for further corrosion by forming a protective film. It may slow down the corrosion process either by increasing anodic or cathodic polarization behavior or by reducing diffusion of ions to the metallic surface. The presence of sufficient concentration of organic inhibitors affects the entire surface of a corroding metal and thus it is designated as film forming inhibitor that protects the metal by forming a hydrophobic film on the metal surface. The effectiveness of these inhibitors depends on the chemical composition, molecular structure, and their affinities for the metal surface. Since, film formation is an adsorption process and it depends on temperature and pressure which is an essential parameter of the system. The organic inhibitors are adsorbed according to presence of ionic charge of the inhibitor and

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the charge on the surface. Cationic inhibitors, such as amines and anionic inhibitors such as sulfonates, are adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors. However determination of optimal concentration for specific inhibitor in a certain corrosive environment is a challenging task. For example, a concentration of 0.05% sodium benzoate is effective in 3.5% sodium chloride solution at a pH value of 7.5. There are numerous chemical inhibitors are available that exhibit inhibitive properties but only few are actually used in practice. This may be due to fact that the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Also, the other parameters such as availability, toxicity, cost and environmental friendliness are of considerable importance.

**Corrosion Costs and Preventive Strategy**

Despite many developments in corrosion resistant alloys over the past few decades, carbon steel still constitutes an estimated 80-90% of the material used in the oil industry. It is usually the most cost effective option, being a factor of 3 to 5 times cheaper than stainless steels. Yet its corrosion resistance is poor in aggressive environments, and the cost savings can only be realized by adding a suitable corrosion inhibitor to the environment or to the steel surface. Inhibitors are used in a wide range of applications such as oil and gas exploration and production industry, the petroleum refining industry, the chemical industry, heavy industrial manufacturing industry, water treatment facilities, and the product additive industries. A particular advantage of corrosion inhibition is that it can be implemented in situ without disrupting a process. The largest consumption of corrosion inhibitors is in the oil industry, particularly in the petroleum refining industry. The total consumption of corrosion inhibitors in the United State has doubled from approximately $600 mn in 1982 to nearly $1.1 bn in 1998.

**Inhibitor Efficiency**

A corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of that inhibitor is thus expressed by a measure of this improvement known as inhibitor efficiency and expressed as:

\[
\text{Inhibitor efficiency (\%)} = 100 \times \frac{(C_{\text{Runinhibited}} - C_{\text{Rinhibited}})}{C_{\text{Runinhibited}}}
\]

where: \(C_{\text{Rinhibited}}\) = corrosion rate in uninhibited condition and \(C_{\text{Runinhibited}}\) = corrosion rate of the inhibited condition. In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration, e.g., a typically good inhibitor may give 95% of inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%.

**Experimental**

The material used in the current study was obtained in a pipe form. The as-received materials was cut into the rectangular specimen of dimension 20 mm x 12 mm x 2.5 mm with a center hole of diameter 1.5 mm at the top edge of each specimen to facilitate the suspension inside of the autoclave of capacity 2.2 liter. The faces of the sample were initially coarse grounded on a SiC belt grinder
machine then consequently machine polished in the successive grades of emery papers (220, 400, 600 800 and 1000). The initial weight and area of the sample was measured using digital weighing machine upto an accuracy of four digits. Four different experiments were carried out at different temperature range (30 °C-120 °C) in an autoclave with a constant partial pressure of 100 psi. All the experiments were carried out for 96 hours in a multiphase dynamic flow loop machine with a constant fluid velocity of 1.5 m/s. The oxygen solubility of the system was maintained below 40 ppm by pouring argon gas inside the vessel. In the beginning of the test, the actual temperature of the machine was set as 30 °C, 60 °C, 90 °C and 120 °C respectively and separately and then created the actual partial pressure of carbon dioxide by releasing the carbon dioxide gas inside the autoclave. After 96 hours of exposure, the samples were taken out from the autoclave washed in distilled water, rinsed in acetone and then dried in air. After cleaning, the coupons were again re-weighed and finally the corrosion rate of the sample was measured in mills per year. The same process was repeated with addition of different concentration of imidazoline inhibitor in the solution. Also, the morphology of the exposed samples was analyzed using different characterization techniques such as Fourier Transform Infra Red (FTIR), Electrochemical Impedance Spectroscopy (EIS) and scanning electron microscopy.

RESULTS AND DISCUSSION
The weight loss graph indicates that the corrosion rate of steel increases with increasing temperature upto 90 °C as shown in Figure 1. This may be due to formation of porous non-protective film on the metal surface results in continuous dissolution in the solution. Beyond this temperature, the corrosion rate again fall down due to formation of dense and adhered layer of oxide iron carbonate film on the metal surface. At higher temperature the formed iron carbonate film is very dense and compact on the surface results in slower corrosion rate. The addition of inhibitors in the solution indicated effectively decrease in the corrosion rate as shown in Figure 1 due to formation of more dense and protective film on the metal surface. The addition of inhibitor on the metal surface showed better performance of protectiveness at all the concentrations. However, the maximum protection was observed at the concentration of 40 ppm where the curve becomes almost saturated and occupies more space as semicircle (Figure 3). This is due to the formation of dense and adhered protective film on the metal surface. The FTIR pattern in Figure 2 indicated the presence of nitrogen based amines in the base inhibitor. EIS pattern also indicted the formation of protective film on the metal surface as the concentration of inhibitor increases upto 40 ppm. In the range of 40-50 pm of imidazoline inhibitor had shown better formation of protective film (Figure 3). The SEM micrographs of exposed sample without application of inhibitor showed the formation and propogation of cracks at the center as shown in Figure 5, while in addition of 40 ppm inhibitor no cracks observed as clearly seen in Figure 6. This may be due to formation of dense and adhered film predominantly forming over the surface and protective in nature.
Table 1: Chemical Composition of as Received Material (wt%) Obtained by Mass Spectroscopy

<table>
<thead>
<tr>
<th>Elements</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
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</tr>
<tr>
<td>Mn</td>
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<tr>
<td>Si</td>
<td>0.31</td>
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<tr>
<td>S</td>
<td>0.003</td>
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<tr>
<td>P</td>
<td>0.004</td>
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<tr>
<td>Cr</td>
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<tr>
<td>Mo</td>
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</tr>
<tr>
<td>Cu</td>
<td>0.14</td>
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</tbody>
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Figure 1: Corrosion Rate Pattern with and Without Inhibitor

Figure 2: FTIR Pattern of Base Imidazoline Inhibitor

Figure 3: EIS Patterns of Steel with and Without Inhibitor

Figure 4: Bode Patterns of API X-52 Grade Steel

Figure 5: SEM Micrograph of Exposed Sample Without Inhibitor
CONCLUSION

The corrosion rate of steel without inhibitor had shown higher corrosion rate while addition of imidazoline inhibitor in all the concentrations reduced the corrosion rate significantly. The more protection has been observed at 40 ppm of imidazoline due to formation of dense and adhered layer of protective film on the metal surface. At aggressive temperature the layer formed on the surface dissolving continuously and the reaction rate becomes faster and shown higher corrosion rate while at higher temperature the iron carbonate film form in presence of nitrogen based imidazoline inhibitor which is very dense and compact on the metal surface results in slower corrosion rate.

REFERENCES


