Inhibitive Assessment of Stearamide as a Corrosion Inhibitor for Mild Steel in HCl Solution

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In this study effect of Stearamide as a corrosion inhibitor for mild steel in hydrochloric acid media was investigated employing various electrochemical techniques include potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR). In view of the fact that Stearamide is an insoluble compound in water, its inhibitive effect was examined by dissolving 1000ppm of it into an organic solvent followed by immersing of steel surface into the solution for 7, 15, 30 and 60 minutes. As a result of the immersion of steel into the solution, the Stearamide was allowed to be adsorbed on the surface and its corrosion inhibition was investigated by moving the sample into a 0.1M HCl solution and employing several electrochemical techniques. Such a method of inhibitor adsorption is regularly used during corrosion inhibitor injection into the gas well tubing. The results of investigation show that Stearamide acts as adsorptive inhibitor, reduces anodic dissolution and also retards the hydrogen evolution reaction via blocking the active reaction sites on the metal surface. Additionally, it was illustrated that Isopropyl alcohol is a more beneficial solvent for Stearamide as compared to dimethyl sulfoxide (DMSO). Isopropyl alcohol acts as inhibitor itself and its mixture with Stearamide has synergistic effect on corrosion inhibition. The optimal condition of immersing steel into the solution was 15min immersion of mild steel in both solutions, and the inhibition efficiency was approximately 90% when Isopropyl alcohol was used as the solvent. EIS investigation demonstrates that the thickness of protective layer formed on metal surface by Isopropyl alcohol solution is almost 5 times higher than that formed by DMSO.

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1. INTRODUCTION

Mild steel is widely applied as the constructional material in many industries owing to its excellent mechanical properties and low cost. As some of the important fields of application are acid pickling, industrial cleaning, acid descaling, oil-well acidizing and petrochemical processes, the main problem of mild steel is its dissolution in acidic solutions. Several methods are commonly used for corrosion prevention. Utilizing inhibitors is one of the cost-effective protection methods of metals and alloys in acids such as hydrochloric acid [1-5]. Inhibitors are, in general, organic compounds which have nitrogen, oxygen and sulfur in their molecular structure [1-12]. The inhibiting effect is generally explained by the formation of a physical and/or chemical adsorption film barrier on the metal surface [7,13]. Physiosorption involves electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at metal/solution interface. Chemisorption, involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type bond. In fact, electron transfer is normally for transition metals having vacant low-energy electron orbitals. Chemisorption is characterized by much stronger adsorption energy than physical adsorption. Organic molecules could be adsorbed on the metal surface by one of the following four mechanisms (a) electrostatic interaction between charged surface of metal and the charge of the inhibitor, (b) interaction of unshared electron pairs in the inhibitor molecule with the metal, (c) interaction of p-electron with metal, and (d) a combination of the (a–c) types [14,15]. Stearamide is one of the stearic acid derivatives which is usually used in powder metallurgy processes as a lubricant to reduce applied stress in powder compressing [16,17]. It is reported that stearic acid and its derivatives are corrosion inhibitors [18]. The purpose of this study is assessment of the inhibitive capabilities of Stearamide as a corrosion inhibitor for mild steel in hydrochloric acid media.

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2. EXPERIMENTAL

Figure 1 shows molecular structure of Stearamide. A rod of mild steel with chemical composition of (in wt%) 0.16%C, 0.1%Si, 0.4%Mn, 0.02%S, 0.13% and Fe balance was used as a working electrode. The reference electrode was a saturated calomel electrode (SCE), and a foil of platinum was used as counter auxiliary electrode. The electrolyte solution was 0.1M HCl. Since Stearamide is insoluble in water even by using intermediary solvent, two 1000ppm solutions of Stearamid in Demethyl sulfoxid (DMSO) and Isopropyl alcohol in which Stearamide dissolved completely were prepared. The working electrode (steel surface) was immersed into the solution (prepared admixture of solvent and Stearamide) for different times with the purpose of adsorption of Stearamide on steel surface. For this purpose, initially, working electrode was polished to 1000 grit SiC and after degreasing with acetone and washing by distilled water, it was immersed into the solution containing Stearamide. After immersion time of 7, 15, 30 and 60 minute, the electrode was removed and immersed into 0.1M HCl solution immediately. Several electrochemical techniques were employed in order to identify behavior of mild steel.

![Figure 1. Molecular structure of Stearamide](image)

Before each experiment, the working electrode was immersed in the cell for 20 minutes to reach the open circuit potential in a steady state condition. Potentiodynamic polarization curves were recorded at constant sweep rate of 1mV/s. The scanning range was from -200 to +200 mV around the open circuit potential. All tests were carried out at ambient temperature. EIS measurements were carried out in frequency range of 30 kHz to 10 MHz with amplitude of 15 mV peak-to-peak using AC signals at open circuit potential. Linear polarization resistance (LPR) was also achieved by polarizing the specimen in different conditions from -15mV to +15mV by 10mV/min scan rate. The LPR value was measured by calculating the slope of current-potential plot. Electrochemical tests were conceded by means of Gill AC automated potentiostat (ACM Instruments).

3. RESULTS AND DISCUSSION

3.1. Tafel Polarization  
Cathodic and anodic polarization plots of mild steel immersed in 0.1M HCl at ambient temperature with different exposure times in DMSO and alcohol solutions are shown in Figure 2. Electrochemical parameters include corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$). Cathodic and anodic Tafel slopes ($\beta_c$ and $\beta_a$) were measured by Tafel extrapolating of the anodic and cathodic lines, and are listed in Table 1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time (min)</th>
<th>LPR (Ω cm$^2$)</th>
<th>%η</th>
<th>%LPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>7</td>
<td>56.87</td>
<td>16.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>71.93</td>
<td>33.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>67.14</td>
<td>28.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>58.78</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>Alcohol</td>
<td>7</td>
<td>284.86</td>
<td>83.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>321.51</td>
<td>85.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>154.44</td>
<td>69.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>70.701</td>
<td>32.5</td>
<td></td>
</tr>
</tbody>
</table>

The degree of surface coverage ($\theta$) and the percentage of inhibition efficiency ($%\eta$) were calculated using the following equations [3,10,19]:

$$\theta = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100$$  \hspace{1cm} (1)

$$%\eta = \frac{\theta}{100}$$  \hspace{1cm} (2)

where $i^0_{corr}$ and $i_{corr}$ are corrosion current densities of mild steel without and with immersing of working electrode in inhibitor solution respectively. From the results in Table 1, it can be seen that the values of corrosion current density ($i_{corr}$) by immersing of mild steel in inhibitor solution is lower than that in no-exposure condition. The corrosion current densities for alcohol solution at all exposure times are lower than that for DMSO solution. This indicates more beneficial effect of alcohol on adsorption of Stearamide on mild steel than DMSO. Figure 2 shows decrease in anodic and cathodic Tafel slopes for both inhibitors in all concentrations.

Although in both solvents, Stearamide is adsorbed on metal surface, however, no important changes in Tafel slope could be observed. Therefore, the inhibition role of this compounds is not through the interference on the reactions of metal dissolution and reduction of protons [20]; and Stearamide acts as adsorptive inhibitor, i.e., it reduces anodic dissolution and also retards the hydrogen evolution reaction by blocking the active reaction sites on the metal surface or adsorbed molecules, mechanically screens the coated part of the electrode and therefore, protects it from the action of the corrosion medium [2]. Figure 3 shows this phenomenon schematically. As it was discussed earlier, Stearamide is
insoluble in water. This behavior of Stearamide arises from its dual characteristics.

As it is obvious in Figure 1, Stearamide has two different properties in its molecular structure. A side which contains oxygen and nitrogen atoms is polar (hydrophilic character) due to unshared electron pairs of oxygen and nitrogen, and the other side does not have polarity (hydrophobic character). Since the non-polar side of Stearamide molecule is much stronger than its polar side, and on the other hand hydrogen bond in water molecules is strong, Stearamide is insoluble in water. However, in components like isopropyl alcohol and DMSO, hydrogen bond is not as strong as water molecules, and as a result Stearamide is dissolved completely in these solvents [21-22]. But, by immersing the metal surface in these solutions which contain Stearamide, this component can be adsorbed on the metal surface. In adsorption stage, as it can be seen in Figure 3.a, by interaction between electrostatic charges on metal surface and unshared electron pairs of oxygen and nitrogen atoms in Stearamide molecule (polar side of molecule), a protective layer is formed on the surface. The other side of molecule has hydrophobic character, and therefore, this protective layer is an insulated layer on those parts of metal surface that is covered (Figure 3.b). This insulated protective layer in acid solution can block the active reaction sites in which iron dissolution or hydrogen evolution occurs, as it was explained above.

To evaluate the effect of pure DMSO and alcohol on corrosion inhibition of mild steel, working electrode was immersed into DMSO and alcohol for 30min. Figure 4 shows the potentiodynamic polarization results in 0.1M HCl after 30min. immersing of mild steel into DMSO and alcohol.

It is obvious that alcohol has beneficial effect on corrosion behavior, but DMSO has no considerable effect. In fact, alcohol mainly acts as a cathodic inhibitor, while DMSO partially accelerates anodic dissolution. In contrast, it was illustrated above that immersing in alcohol solution has more advantageous effect on corrosion behavior than DMSO solution and alcohol is an inhibitor itself. The synergism parameter ($S$) was calculated according to the following formula [23-26]:

$$S = \frac{\text{Inhibition efficiency of DMSO + Alcohol}}{\text{Inhibition efficiency of DMSO}}$$
where \( \eta_1 \) and \( \eta_2 \) is efficiency of each inhibitor, and \( \eta_{1.2} \) is efficiency in the presence of both inhibitors. If \( S=1 \) there is no interaction between the two inhibitors, while, when \( S>1 \), inhibitors have synergistic effect, and \( S<1 \) indicates inhibitor combination has deteriorative effect. In this case, in view of the fact that corrosion behavior in the presence of only Stearamide cannot be detected on one hand, and DMSO has no helpful effect on corrosion behavior on the other hand, consequently, decrease in corrosion current density as a result of immersing in DMSO solution containing Stearamide can be attributed to Stearamide only. Corrosion current density by 30 min immersing in pure alcohol is 0.3245 mA/cm\(^2\), and therefore, the \( S \)-value will be 1.141. This indicates the synergistic effect of combination of Stearamide and Isopropyl alcohol. This phenomenon is attributable to stabilization of adsorbed Stearamide by means of electrostatic interactions with the alcohol molecules, resulting in greater surface coverage [23].

3.2 Electrochemical Impedance Spectroscopy (EIS) The result of the EIS measurement was figured by Nyquist plots (see Figure 5). The capacitive loop was related to charge transfer in corrosion process [27]. Nyquist plots are similar and show a simple semicircle in DMSO solution.

\[
S = \frac{1 - \eta_1 - \eta_2}{1 - \eta_{1.2}} \tag{3}
\]

In alcohol solution, Nyquist plots show two capacitive loops. First, at higher frequencies can be attributed to formed inhibitor layer on surface and second, at lower frequencies are due to charge transfer layer. Two equivalent circuits used to fit the EIS data of mild steel are shown in Figure 5 as inserted micrographs.

According to the above-mentioned equivalent circuits, the solution resistance \( (R_s) \), the charge transfer resistance \( (R_{ct}) \) and the constant phase element \( (\text{CPE}) \) were extracted and listed in Table 2. The \( R_{ct} \) values increased with increasing the exposure time in both solutions from 7 to 15 minutes, indicating formation of an insulated adsorption layer [14]. By increasing exposure time from 15 to 60 minutes, this insulated layer was broken down and therefore, charge transfer resistance decreases. Inhibitor efficiency can also be estimated by charge transfer resistance according to the following formula [28]:

\[
\%\eta = \frac{R^0 - R_s}{R} \times 100 \tag{4}
\]

where \( R^0 \) and \( R \) are charge transfer resistance of mild steel without and with immersing in inhibitor solution respectively. Table 2 shows these values of efficiency and sindsicates close correlation with those of polarization results. Both polarization and EIS results show that the efficiency of alcohol solution is higher than DMSO solution in all exposure times.

CPE was used as the alternate for capacitor to fit impedance behavior of the electric double layer more accurately. The impedance of the CPE is expressed as [29]:

\[
Z_{cpe} = \frac{1}{P(i\omega)^n} \tag{5}
\]

where \( P \) is the magnitude of the CPE; \( \omega \) the angular frequency; \( n \) as the deviation parameter \((-1 \leq n \leq 1 \) which is dependent on the surface morphology). The higher frequency range loops have depressed semicircular appearance, \( 0.5 \leq n \leq 1 \), which is often referred to as frequency dispersion as a result of the non-homogeneity or the roughness of the solid surface [30-31] or time delaying during EIS measurement. The capacitive loop, \( R_{ct} \)–CPE, could be attributed to the charge transfer reaction. For a circuit including a CPE, the double layer capacitance \( (C_{dl}) \) can be calculated from CPE parameter values \( P \) and \( n \) using the expression [32]:

\[
C_{dl} = \frac{P\omega^{n-1}}{\sin(n(\pi/2))} \tag{6}
\]

According to the definition of the layer capacitance presented in the Helmholtz model, the capacitance is inversely proportional to the surface film thickness [33].

\[
C_{dl} = \frac{\varepsilon_{dl} \varepsilon}{d} \tag{7}
\]

where \( d \) is the thickness of the film, \( S \) is the surface of the electrode, \( \varepsilon_{dl} \) is the permittivity of the air and \( \varepsilon \) is the local dielectric constant. The decrease in \( C_{dl} \) by
increasing exposure time from 7 to 15 minutes is due to the steady replacement of water molecules by the adsorption of the inhibitor molecules at metal/solution interface, which is leading to a protective film on the steel surface and increasing of \( d \) value. Increase in \( C_{dl} \) by increasing time exposure from 15 to 60 minutes can be attributed to failure of formed protective layer on surface. Furthermore, in similar exposure times the value of \( C_{dl} \) for alcohol solution is lower than that for DMSO solution, indicating a superior protective layer in alcohol solution. For instance, the value of \( C_{dl} \) for alcohol solution is approximately 5 times lower than that for DMSO solution in 15 minutes exposure time, indicating layer in alcohol solution is thickened 5 times higher than that formed by DMSO solution. In fact, as it is elucidated above, alcohol has synergistic effect and it is inhibitor as well. Hence, combination of Stearamide and alcohol increases inhibition efficiency more than each component alone.

### 3.3. Liner Polarization Resistance (LPR)

Figure 6 shows the liner polarization resistance (LPR) results for both solutions in different exposure times. Surface coverage and inhibitor efficiency were calculated according to the Eq. 4 and are listed in Table 3.

Figure 6 shows that by increasing the exposure time from 7 to 15 minutes, LPR value increases, and by increasing time from 15 to 60 minutes, LPR value decreases.

![Figure 6. Liner polarization resistance (LPR) results for both solutions versus exposure time](image)

Comparable to the results of polarization and EIS measurement, the values of efficiency of both solutions...
in all exposure times show that by increasing the exposure time from 7 to 15 minutes, efficiency increases. By increasing time from 15 to 60 minutes efficiency decreased, and also it has higher value for alcohol than DMSO, showing more beneficial effect of alcohol as a solvent on corrosion protection of mild steel in HCl medium by Stearamide as an inhibitor. The synergism parameter can also be calculated from LPR results. Considering LPR value of 89.411 Ω.cm² for immersion of metal surface in pure alcohol for 30 minutes, the efficiency value of alcohol is 46.616 Ω.cm², and by using Eq. 3 and data in Table 3, the S-value will be 1.094. This value indicates the synergistic effect of combination of Stearamide and alcohol as well.

4. CONCLUSION

Effect of Stearamide as an inhibitor by immersing mild steel in 10000ppm solution of Stearamide into two solvents, namely DMSO and Isopropyl alcohol, was investigated and following results was obtained:

1. Stearamide shows inhibition properties in hydrochloric acid by adsorption on metal surface.
2. The profitable exposure time was 15 minutes in both solutions and values of efficiency were 90% for alcohol solution and 83% for DMSO solution respectively.
3. Stearamide acts as adsorptive inhibitor, it reduces anodic dissolution and also retards the hydrogen evolution reaction via blocking the active reaction sites on the metal surface.
4. Since both Stearamide and alcohol show inhibition properties, the electrochemical results indicate that their combination has synergistic effect and the value of synergism parameter was 1.141

5. ACKNOWLEDGMENT

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6. REFERENCES

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In this study, the inhibitive behavior of stearamide on carbon steel was investigated in a 10% HCl solution. Stearamide was applied as an inhibitor in the form of a solution and the corrosion inhibition efficiency was evaluated using electrochemical techniques such as cyclic voltammetry and impedance measurements. The results showed that stearamide is an effective corrosion inhibitor for mild steel in hydrochloric acid solution. The inhibition efficiency increased with increasing concentration of stearamide.


