List of Publications


5. M. Mobin and Mosarrat Parveen, “Inhibition of Mild Steel Corrosion in Acidic Medium Using L-Cystine and Surfactants Additives”, Accepted for presentation in International Corrosion Conference and Expo, CORCON 2012, to be held during September 26th - 29th, 2012 at Goa, India.

7. M. Mobin and Mosarrat Parveen, “Corrosion Inhibition Behavior of L-Cystine on Mild Steel in 0.1 M H₂SO₄ and Synergistic Influence of Sodium Dodecyl Sulfate and Cetyltrimethyl Ammonium Bromide,” Acta Chimica Slovenica (ACSi), Communicated.
Published Papers
Inhibition of Mild Steel Corrosion Using L-tryptophan and Synergistic Surfactant Additives

M. Mobin,* Mosarrat Parveen, M. Alam Khan

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh, India-202 002 (India)

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Abstract

The corrosion inhibition characteristics of nitrogen containing amino acid L-tryptophan on mild steel in 0.1 M HCl solution, in the temperature range of 30-50 °C, was studied by weight loss and potentiodynamic polarization measurements. L-tryptophan significantly reduces the corrosion rates of mild steel; the maximum inhibition efficiency being 83% at 50 °C in presence of inhibitor concentration of 500 ppm. The effect of the addition of very small concentrations of anionic surfactant, sodium dodecyl sulfate (SDS), and of cationic surfactant, cetyl trimethyl ammonium bromide (CTAB), on the corrosion inhibition behavior of L-tryptophan was also studied. The inhibition efficiency (IE) of L-tryptophan significantly improved in presence of both surfactants. The effect of SDS and CTAB on the corrosion inhibition behavior of L-tryptophan appears to be synergistic in nature, the values of synergism parameter being greater than unity. The adsorption of inhibitors on mild steel surface obeyed Langmuir’s adsorption isotherm. The calculated thermodynamic parameters for adsorption reveal a strong interaction between the inhibitors and the mild steel surface. The results obtained by electrochemical studies are consistent with the results of the weight loss measurements. L-tryptophan acts more anodic than cathodic inhibitor.

Keywords: L-tryptophan, corrosion inhibitor, adsorption, surfactants, electrochemical technique.

Introduction

Among the several methods to save the metals from corrosion, the use of inhibitors has found wide attention both in academia and industries. The corrosion inhibitors are generally used to protect metals against the attack of the acid solutions, which are widely used in acid pickling, industrial cleaning, acid descaling, oil-well acidizing, etc. Organic compounds containing nitrogen, sulfur

* Corresponding author. E-mail address: drmmobin@hotmail.com
and oxygen have been widely used as potential corrosion inhibitors in acid solutions [1-3]. These compounds prevent corrosion either by getting adsorbed, or by forming a protective layer or an insoluble complex on the metal surface, thus blocking the active corrosion sites. However, most of the organic compounds are synthetic chemicals, expensive and very hazardous to both human beings and the environments, and need to be replaced by non-toxic and environmental friendly compounds.

In recent years, a number of eco-friendly compounds such as extract of common plants which contain many organic compounds, e.g., alkaloids, fatty acids, carbohydrates, tannins, pigments and amino acids, have been exploited as green alternative to toxic and hazardous compounds [4]. The amino acids which contain carboxyl and amino functionalities bonded to the same carbon atom are non-toxic, relatively cheap and easy to produce in purities greater than 99%. It has been shown by various authors that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds as substitutes to conventional corrosion inhibitors that are usually toxic [5-9]. The inhibition effect of three amino acids, namely, alanine, glycine and leucine, against steel corrosion in HCl solutions has been investigated by potentiodynamic polarization method. The inhibition effect was found to range from 28-91% [10]. The corrosion inhibition of Fe in 1 M HCl using twenty two different common amino acids and four related compounds has been investigated using potentiodynamic polarization curves [11]. In general, amino acids with longer hydrocarbon chains showed greater inhibition. Additional groups or groups which increased electron density on alpha amino group also increased the inhibition efficiency.

The nitrogen containing amino acid L-tryptophan is a derivative of indole. The molecular structure of the compound suggests that it has strong potential to become an effective corrosion inhibitor. Moretti and Guidi [12] reported the corrosion inhibition of L-tryptophan on copper in aerated 0.5 M H$_2$SO$_4$ in the temperature range of 20-50 °C. The corrosion rate did not rise as temperature increased. Recently, corrosion inhibition behavior of low carbon steel by L-tryptophan was investigated using weight loss experiments and Tafel polarization curves [13]. The adsorption behavior of L-tryptophan at Fe surface was also investigated by the molecule dynamics simulation method and density functional theory. The results indicated that L-tryptophan could adsorb on Fe surface through the indole ring with π-electrons and nitrogen/oxygen atom with the lone pair electrons in its molecule.

The majority of the acidic inhibitors have been known for their specificity of inhibition action. A combination of inhibitors is likely to provide multiple effects required for effective corrosion inhibition. The addition of halide ions to organic compounds has shown synergistic effect and resulted in improved inhibition efficiency of many organic compounds, and has been reported in the literature [14]. However, the influence of surfactants on the corrosion inhibition behavior of organic compounds is very scanty [15]. Surfactants have effectively been used as corrosion inhibitors as their molecules possess strong adsorption ability to the metallic surfaces. The adsorbed
molecules form monolayer or bilayer hemimicelles or admicelles, depending upon the surfactant concentration, and prevent the acid to attack the surface, and thus reduce the corrosion attack [16-19]. Amino acids interact with the surfactants to form a complex structure and help to adhere to surface, which offers great promise in corrosion inhibition. The binding of surfactants to amino acids depends upon the structure, molecular weights, interaction times and charge densities. A survey of literature indicates that only limited number of references is available dealing with the corrosion inhibition effect of L-tryptophan on mild steel. Further, the corrosion inhibition effect of amino acids in presence of surfactants has not yet been reported to the best of our knowledge. However, the influence of some surfactants on the corrosion inhibition of some oxidiazoles has recently been reported [15]. The adsorption of oxidiazoles on mild steel surface is reported to be significantly enhanced in presence of surfactants.

The present work was undertaken to investigate the corrosion inhibition behavior of L-tryptophan on mild steel in 0.1 M HCl solution. The effect of the addition of very small concentrations of SDS and CTAB on the corrosion inhibition behavior of L-tryptophan, for which no reference is available in the literature, was also studied. The techniques used are weight loss and potentiodynamic polarization measurements.

**Experimental**

**Material preparation**

Mild steel specimens having composition (weight %): 0.20 % C, 0.53 % Mn, 0.11 % S, 0.036 % Si and 0.098 % P, and balance Fe, were used for corrosion inhibition studies. The inhibitor L-tryptophan [(2S)-2-amino-3-(1-H-indol-3-yl) propanoic acid; molecular mass 204.23 g mole$^{-1}$], anionic surfactant, sodium dodecyl sulfate (SDS), cationic surfactant, N-cetyl N,N,N-trimethyl ammonium bromide (CTAB) (CDH, India), were used as received. The other chemicals used were all reagent grade. The stock solution of HCl and inhibitors were prepared using double distilled water.

**Weight loss measurements**

Mild steel coupons of dimension 2.5 × 2.0 × 0.03 cm were used for weight loss measurements. The coupons were machined and abraded on different grit SiC papers and finally washed and degreased using acetone, and dried up. To hold the specimens a hole of 1.5 mm dia was made near the edge. The weight loss studies were carried out in the temperature range of 30-50 °C in 0.1 M HCl. The test solution was made of AR grade 35% HCl using double distilled water. The concentration of L-tryptophan was kept between 1 to 500 ppm in HCl. The weight loss experiments were performed for duration of 6 h, as per ASTM designation G1-90. The inhibition efficiency (%IE) was calculated by using the following equation:
\[
\% \text{IE} = \frac{CR_o - CR_i}{CR_o} \times 100 \tag{1}
\]

where, \( CR_o \) = corrosion rate of mild steel in blank HCl; \( CR_i \) = corrosion rate of mild steel in presence of the inhibitor.

**Potentiodynamic polarization measurements**

The potentiodynamic polarization measurements were carried out using an EG and G potentiostat/galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG and G; model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and steel coupons as working electrode. The experiments were performed using a scan rate of 0.166 mV/S, commencing at a potential above 250 mV more active than the stable open circuit potential. All the measurements were carried out at room temperature (30 ± 1 °C). Before starting the measurements the specimen was left to attain a steady state indicated by a constant potential. The inhibition efficiency was calculated using the relationship:

\[
IE(\%) = \left(1 - \frac{i_{corr}}{i_{corr}^o}\right) \times 100 \tag{2}
\]

where \( i_{corr} \) = inhibited current density and \( i_{corr}^o \) = uninhibited current density.

**Table 1.** Corrosion parameters for mild steel in 0.1 M HCl in absence and presence of L-tryptophan at 30-50 °C from weight loss measurements.

<table>
<thead>
<tr>
<th>L-tryptophan Conc. (ppm)</th>
<th>30 °C</th>
<th>40 °C</th>
<th>50 °C</th>
<th>30 °C</th>
<th>40 °C</th>
<th>50 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>102.14</td>
<td>253.62</td>
<td>874.47</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>57.42</td>
<td>131.32</td>
<td>551.57</td>
<td>44.29</td>
<td>47.98</td>
<td>36.15</td>
</tr>
<tr>
<td>50</td>
<td>55.03</td>
<td>101.46</td>
<td>348.80</td>
<td>46.43</td>
<td>60.12</td>
<td>60.14</td>
</tr>
<tr>
<td>100</td>
<td>47.68</td>
<td>80.25</td>
<td>207.21</td>
<td>53.57</td>
<td>68.21</td>
<td>76.18</td>
</tr>
<tr>
<td>200</td>
<td>46.93</td>
<td>78.79</td>
<td>200.94</td>
<td>54.29</td>
<td>68.79</td>
<td>76.86</td>
</tr>
<tr>
<td>400</td>
<td>42.53</td>
<td>88.46</td>
<td>154.01</td>
<td>58.57</td>
<td>65.32</td>
<td>82.26</td>
</tr>
<tr>
<td>500</td>
<td>36.67</td>
<td>75.52</td>
<td>146.67</td>
<td>64.29</td>
<td>70.23</td>
<td>83.11</td>
</tr>
</tbody>
</table>

**Results and discussion**

**Weight loss measurements**

The corrosion of mild steel in 0.1 M HCl in absence and presence of different concentrations of amino acid L-tryptophan was studied in the temperature range of 30-50 °C using weight loss technique. Table 1 shows the calculated values of weight loss, corrosion rate and IE at different concentrations of L-tryptophan.
under different temperatures. From these data it is clearly seen that the corrosion rate of mild steel depends upon two factors, namely inhibitor concentration and temperature. The corrosion rates are significantly reduced in presence of L-tryptophan. The maximum increase in IE of 64% was observed at a concentration of 500 ppm at 30 °C, which further increased to 83% on increasing the temperature from 30 to 50 °C. The plots of IE as a function of L-tryptophan concentration, at 30-50 °C, reveal that IE increases with increase in concentration (Fig. 1a).

![Graph a)

![Graph b)

![Graph c)

**Figure 1.** Plots of inhibition efficiency (IE) vs. inhibitor concentration for mild steel in 0.1 M HCl at different temperatures: (a) L-tryptophan; (b) L-tryptophan + SDS; (c) L-tryptophan + CTAB.
**Table 2.** Calculated values of corrosion rate, inhibition efficiency and synergism parameter for mild steel in 0.1 M HCl in the absence and presence of different concentrations of L-tryptophan with SDS at 30-50 °C, from weight loss measurements.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (% I)</th>
<th>Synergism parameters ($S_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L-tryptophan</td>
<td>SDS</td>
<td>30 °C</td>
</tr>
<tr>
<td>Blank</td>
<td>Blank</td>
<td>102.39</td>
<td>253.62</td>
</tr>
<tr>
<td>-</td>
<td>1</td>
<td>87.55</td>
<td>196.51</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>48.62</td>
<td>97.69</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>44.00</td>
<td>89.82</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>42.53</td>
<td>80.67</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>41.07</td>
<td>88.46</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>30.80</td>
<td>79.20</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>36.67</td>
<td>66.00</td>
</tr>
</tbody>
</table>

Except at very low concentration of L-tryptophan (up to 10 ppm), IE increases with increasing temperature. The inhibition behavior of L-tryptophan on mild steel in 0.1 M HCl can be attributed to the adsorption of the molecules on the steel surface. The effectiveness of the adsorption of L-tryptophan may be attributed to the presence of two nitrogen atoms in the molecule and its large volume [20]. The increased IE with increasing the inhibitor concentration indicates that more inhibitor molecules are adsorbed on the steel surface, leading

**Table 3.** Calculated values of corrosion rate, inhibition efficiency and synergism parameter for mild steel in 0.1 M HCl in the absence and presence of different concentrations of L-tryptophan with CTAB at 30-50 °C, from weight loss measurements.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (% I)</th>
<th>Synergism parameters ($S_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L-tryptophan</td>
<td>CTAB</td>
<td>30 °C</td>
</tr>
<tr>
<td>Blank</td>
<td>Blank</td>
<td>102.14</td>
<td>253.62</td>
</tr>
<tr>
<td>-</td>
<td>1</td>
<td>53.01</td>
<td>99.22</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>38.13</td>
<td>99.22</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>35.57</td>
<td>90.34</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>35.57</td>
<td>56.91</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>34.83</td>
<td>56.03</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>24.93</td>
<td>51.60</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>23.47</td>
<td>55.45</td>
</tr>
</tbody>
</table>
The increase in IE with increasing temperature suggests that at higher concentrations L-tryptophan is chemically adsorbed on to the mild steel surface. At lower concentrations the adsorbed film is not so stable and gets damaged at higher temperature, thus showing lower IE. The amino acid, L-tryptophan is easily protonated and expected to involve two ways of adsorption. Firstly, it may be adsorbed via donor-acceptor interactions between the \( \pi \) electrons of the indole rings and the unshared electron pairs of the heteroatom, to form a bond with vacant d-orbital of the metal surface [22]. Secondly, the –NH\(_2\) group of amino acid in acid medium is readily protonated and might get adsorbed on the metallic surface via the negatively charged acid anions [23].

To observe the effect of SDS and CTAB on the corrosion inhibition behavior of L-tryptophan, the corrosion of mild steel in 0.1 M HCl in absence and presence of different concentrations of L-tryptophan, in combination with 1 ppm of SDS and 1 ppm of CTAB, was separately studied in the temperature range of 30-50 °C by weight loss technique. The results are shown in Tables 2 and 3. The corrosion rates of mild steel in 0.1 M HCl in presence of L-tryptophan in combination with surfactants is further reduced in comparison to L-tryptophan alone. Fig. 1b and 1c show the plots of IE as a function of concentration of L-tryptophan in combination with 1 ppm of SDS and CTAB, respectively, at 30-50 °C.

**Table 4.** Thermodynamic parameters for corrosion of mild steel in absence and presence of L-tryptophan and surfactants.

<table>
<thead>
<tr>
<th>L-tryptophan conc. (ppm)</th>
<th>Surfactant conc. (ppm)</th>
<th>( \Delta H ) (kJmol(^{-1}))</th>
<th>( -\Delta S ) (jk(^{-1})mol(^{-1}))</th>
<th>- Q (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>86.54</td>
<td>78.49</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>0.0</td>
<td>54.95</td>
<td>33.76</td>
<td>41.8</td>
</tr>
<tr>
<td>500</td>
<td>1 (SDS)</td>
<td>61.81</td>
<td>11.62</td>
<td>33.51</td>
</tr>
<tr>
<td>500</td>
<td>1 (CTAB)</td>
<td>72.47</td>
<td>20.09</td>
<td>18.19</td>
</tr>
</tbody>
</table>
Considering the effect of surfactants on the corrosion inhibition behavior of L-tryptophan, the anionic SDS binds with L-tryptophan through electrostatic interaction, thus helps to adsorb at the metal surface more firmly and displays higher IE. The IE of L-tryptophan in presence of 1 ppm of CTAB is also higher, but lower in comparison to SDS.

Figure 3. Arrhenius plot for log CR/T vs. 1/T (♦ Blank; ■ L-tryptophan; ▲ L-tryptophan + SDS; ● L-tryptophan + CTAB).

It may be due to the adsorption of L-tryptophan to metal surface by binding with CTAB as co-ions or through hydrophobic interaction. The effect of surfactants on the IE of L-tryptophan in 0.1 M HCl appears to be synergistic in nature. The values of the synergism parameter $S_1$ for various concentrations of L-tryptophan in combination with 1 ppm of surfactants were calculated from the gravimetric data at 30 °C using the relationship [14]

$$S_1 = \frac{1-I_{1+2}}{1-I_{1+2}'}$$

where, $I_{1+2} = (I_1 + I_2)$; $I_1$ is IE of L-tryptophan; $I_2$ is IE of the surfactants; and $I_{1+2}'$ being IE of L-tryptophan is in combination with surfactants. The results are given in Tables 2 and 3. The values are all greater than unity. This is an indication that the enhanced IE resulting from the addition of surfactants to L-tryptophan is synergistic in nature and proved that addition of a very small concentration of surfactants can improve the adsorption of L-tryptophan on the mild steel.

The inhibition of mild steel corrosion in presence of various organic compounds has been attributed to their adsorption on the steel surface, being generally confirmed from the fit of the experimental data to various adsorption isotherms. The degree of surface coverage ($\theta$) for various concentrations of L-tryptophan, and L-tryptophan in combination with 1 ppm of SDS and CTAB, in 0.1 M HCl at 30-50 °C, for 6 h immersion time, has been evaluated by weight loss measurements. The data were tested graphically by fitting to various isotherms and the best result was obtained for Langmuir adsorption isotherm.
Table 5. Thermodynamic parameters for mild steel in 0.1 M HCl in presence of L-tryptophan and surfactants.

<table>
<thead>
<tr>
<th>Inhibitor conc. (mol dm$^{-3}$)</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-tryptophan 0.10</td>
<td>29.69</td>
<td>32.28</td>
<td>34.38</td>
</tr>
<tr>
<td>L-tryptophan 0.20</td>
<td>28.01</td>
<td>30.55</td>
<td>32.61</td>
</tr>
<tr>
<td>L-tryptophan 0.40</td>
<td>26.70</td>
<td>28.33</td>
<td>31.66</td>
</tr>
<tr>
<td>L-tryptophan 0.50</td>
<td>26.74</td>
<td>28.33</td>
<td>31.21</td>
</tr>
<tr>
<td>SDS + L-tryptophan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001 + 0.10</td>
<td>30.20</td>
<td>32.28</td>
<td>34.85</td>
</tr>
<tr>
<td>0.001 + 0.20</td>
<td>28.59</td>
<td>29.31</td>
<td>33.67</td>
</tr>
<tr>
<td>0.001 + 0.40</td>
<td>27.96</td>
<td>28.74</td>
<td>30.48</td>
</tr>
<tr>
<td>0.001 + 0.50</td>
<td>26.75</td>
<td>28.81</td>
<td>30.67</td>
</tr>
<tr>
<td>CTAB + L-tryptophan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001 + 0.10</td>
<td>30.96</td>
<td>33.49</td>
<td>33.15</td>
</tr>
<tr>
<td>0.001 + 0.20</td>
<td>29.29</td>
<td>31.78</td>
<td>33.14</td>
</tr>
<tr>
<td>0.001 + 0.40</td>
<td>28.69</td>
<td>30.25</td>
<td>31.90</td>
</tr>
<tr>
<td>0.001 + 0.50</td>
<td>28.32</td>
<td>29.39</td>
<td>31.37</td>
</tr>
</tbody>
</table>

Figure 4. Potentiodynamic polarization curves of mild steel in 0.1 M HCl in absence and presence of different concentrations of L-tryptophan: (1) Blank; (2) 100 ppm; (3) 200 ppm; (4) 500 ppm.

Figure 5. Potentiodynamic polarization curves for mild steel in 0.1 M HCl in absence and presence of L-tryptophan and SDS: (1) Blank; (2) L-tryp 100 ppm + SDS 1 ppm; (3) L-tryp 200 ppm + SDS 1 ppm; (4) L-tryp 400 ppm + SDS 1 ppm; (5) L-tryp 500 ppm + SDS 1 ppm.
Figure 6. Potentiodynamic polarization curves for mild steel in 0.1 M HCl in absence and presence of L-tryptophan and CTAB: (1) Blank; (2) L-tryp 100 ppm + CTAB 1 ppm; (3) L-tryp 200 ppm + CTAB 1 ppm; (4) L-tryp 400 ppm+ CTAB 1 ppm; (5) L-tryp 500 ppm+ CTAB 1 ppm.

Table 6. Potentiodynamic polarization parameters for corrosion of mild steel in 0.1 M HCl in absence and presence of various concentrations of L-tryptophan and of L-tryptophan-surfactant mixtures at 30 °C.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>(E_{\text{corr}}) (mV)</th>
<th>(I_{\text{corr}}) (µA)</th>
<th>(\beta_c) (mV)</th>
<th>(\beta_a) (mV)</th>
<th>C.R (mpy)</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-622.96</td>
<td>666.1</td>
<td>283.19</td>
<td>134.63</td>
<td>58.59</td>
<td>-</td>
</tr>
<tr>
<td>L-trypt 100</td>
<td>-614.41</td>
<td>466.8</td>
<td>263.92</td>
<td>116.64</td>
<td>42.76</td>
<td>29.92</td>
</tr>
<tr>
<td>L-trypt 200</td>
<td>-603.23</td>
<td>435.6</td>
<td>271.522</td>
<td>117.146</td>
<td>39.90</td>
<td>34.60</td>
</tr>
<tr>
<td>L-trypt 500</td>
<td>-573.99</td>
<td>170.1</td>
<td>181.23</td>
<td>121.33</td>
<td>15.59</td>
<td>74.46</td>
</tr>
<tr>
<td>SDS 1 + L-trypt 100</td>
<td>-591.88</td>
<td>349.6</td>
<td>255.07</td>
<td>111.37</td>
<td>32.02</td>
<td>47.51</td>
</tr>
<tr>
<td>SDS 1 + L-trypt 200</td>
<td>-582.88</td>
<td>307.1</td>
<td>243.11</td>
<td>106.35</td>
<td>28.13</td>
<td>53.89</td>
</tr>
<tr>
<td>SDS 1 + L-trypt 400</td>
<td>-579.26</td>
<td>204.4</td>
<td>216.94</td>
<td>85.54</td>
<td>18.72</td>
<td>69.31</td>
</tr>
<tr>
<td>SDS 1 + L-trypt 500</td>
<td>-569.54</td>
<td>109.9</td>
<td>206.43</td>
<td>55.75</td>
<td>10.06</td>
<td>83.50</td>
</tr>
<tr>
<td>CTAB1 + L-trypt100</td>
<td>-589.66</td>
<td>438.0</td>
<td>292.43</td>
<td>127.53</td>
<td>40.12</td>
<td>34.24</td>
</tr>
<tr>
<td>CTAB1 + L-trypt200</td>
<td>-581.45</td>
<td>327.7</td>
<td>264.54</td>
<td>120.69</td>
<td>30.02</td>
<td>50.80</td>
</tr>
<tr>
<td>CTAB1+ L-trypt 400</td>
<td>-565.617</td>
<td>171.0</td>
<td>286.99</td>
<td>99.09</td>
<td>15.66</td>
<td>74.328</td>
</tr>
<tr>
<td>CTAB1+ L-trypt 500</td>
<td>-567.777</td>
<td>130.5</td>
<td>285.87</td>
<td>94.42</td>
<td>11.95</td>
<td>80.408</td>
</tr>
</tbody>
</table>

A plot of log \(\theta/1-\theta\) vs.1/T, where T is the solution temperature, was also obtained for L-tryptophan and for L-tryptophan in combination with 1 ppm of surfactants (Fig. 2). The heat of adsorption (\(Q_d\)) was calculated from the slope of the plot (\(-Q_d/2.303R\)) and the values are listed in Table 4. The plot of log (CR/T) vs. 1/T in presence of L-tryptophan and surfactants (Fig. 3) gave a straight line with slope of \((-\Delta H/2.303R\)) and an intercept of \([\log(R/N_h) + (\Delta S/2.303R)]\). The values of \(\Delta H\) obtained from the slope and of \(\Delta S\) evaluated from the intercept, are
given in Table 4. The values of free energy of adsorption ($\Delta G_{ads}$) were calculated using the following equation [24] and are listed in Table 5.

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

(4)

where $K$ is equilibrium constants and is given by

$$K = \frac{\theta}{C(1-\theta)}$$

(5)

where $\theta$ is the degree of surface coverage, $C$ the concentration of the inhibitors in mol dm$^{-3}$, $R$ is the gas constant and $T$ is the solution temperature. The plots of $\log \theta/1-\theta$ vs. $\log C$ showed a linear correlation of slope close to unity, suggesting that the adsorption of L-tryptophan on mild steel surface obeys Langmuir adsorption isotherm. The values of heat of adsorption are less than -40 KJ mol$^{-1}$, suggesting the physical adsorption of the inhibitors [25]. The lower values of $\Delta H$ for L-tryptophan in presence of surfactants indicate less energy barrier for the reaction [26]. The negative values of $\Delta G_{ads}$ suggest that the adsorption of L-tryptophan on mild steel is spontaneous. It is an established fact that values of $\Delta G_{ads}$ around -20 KJ mol$^{-1}$ or less indicate physisorption. The adsorption is attributed to the electrostatic attraction between the charged organic molecules and charged metal surface. The values of $\Delta G_{ads}$ around -40 KJ mol$^{-1}$ or more are considered as chemisorptions. However, the values of $\Delta G_{ads}$ between -20 and -40 KJ mol$^{-1}$ give a disputed judgement about the type of adsorption [27-30]. In the present investigation the values of $\Delta G_{ads}$ are in the range of -26.70 to -34.85 KJ mol$^{-1}$, suggesting a mixed type of adsorption involving both physisorption and chemisorption.

**Potentiodynamic polarization measurements**

Potentiodynamic polarization curves for the corrosion of mild steel in 0.1 M HCl in absence and presence of different concentrations of L-tryptophan, and of L-tryptophan in combination with 1 ppm of SDS and CTAB, are shown in Fig. 4-6. The values of electrochemical parameters as deduced from these curves, e.g., corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), cathodic Tafel slope (bc), anodic Tafel slope (ba) and % inhibition efficiency (% IE), are shown in Table 6. The IE was calculated using the equation:

$$\% \text{IE} = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100$$

(6)

where $i_{corr}^0$ and $i_{corr}$ are the corrosion current density in absence and presence of the inhibitors, respectively. The study of electrochemical data reveals that the value of $i_{corr}$ continuously decreases in presence of L-tryptophan. The maximum IE of about 75% was observed at a concentration of 500 ppm, indicating that a higher coverage of L-tryptophan on steel surface is obtained in the solution with highest concentration of the inhibitor. The values of $E_{corr}$ shift to more positive value compared to the blank, indicating that L-tryptophan acts more as an anodic than a cathodic inhibitor. The addition of 1 ppm of SDS and CTAB to different concentrations of L-tryptophan improved the IE of L-tryptophan significantly.
The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

Conclusions

(1) L-tryptophan showed good performance as corrosion inhibitor for mild steel in 0.1 M HCl, which is further improved in presence of the surfactants SDS and CTAB. The effect of surfactants on corrosion inhibition behavior of L-tryptophan appears to be synergistic in nature.

(2) The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm. The thermodynamic data suggest mixed type of adsorption involving both physisorption and chemisorption.

(3) L-tryptophan acts more as an anodic than a cathodic inhibitor.

References

Inhibition of mild steel corrosion in HCl solution using amino acid L-tryptophan

M. Mobin*, Mosarrat Parveen and M. Alam Khan

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002- India.

Abstract
The corrosion inhibition characteristics of nitrogen containing amino acid L-tryptophan on mild steel in 0.1 M HCl solution was studied by weight loss and potentiodynamic polarization measurements. L-tryptophan significantly reduces the corrosion rates of mild steel; the maximum inhibition efficiency being 83% at 50 °C in presence of inhibition concentration of 500 ppm. The adsorption of inhibitors on mild steel surface obeyed Langmuir’s adsorption isotherm. The calculated thermodynamic parameters for adsorption reveal a strong interaction between the inhibitors and the mild steel surface. The results obtained by electrochemical studies are consistent with the results of the weight loss measurement. L-tryptophan acts more anodic than cathodic inhibitor.

Keywords: Mild steel, Corrosion inhibition, L-Tryptophan, Adsorption, Electrochemical technique.

INTRODUCTION

Organic compounds containing nitrogen, sulfur and oxygen have long been used as potential corrosion inhibitor in acid solutions [1-3]. These compounds get adsorbed, or form a protective layer/insoluble complex on the metal surface and block the active corrosion sites. However, most of these compounds are synthetic chemicals, are expensive and very hazardous to both human beings and the environments and needs to be replaced with nontoxic and eco-friendly compounds. Over the years, numerous classes of organic compounds have been investigated as corrosion inhibitors. However the trend in green chemistry is concentrated towards the replacement of most of these inhibitors with the nontoxic, cheap and eco-friendly compounds.

In recent years, a number of eco-friendly corrosion inhibitors have been exploited as green alternative to toxic and hazardous compound [4-7]. The amino acids which contain carboxyl and amino functionalities bonded to the same carbon atom are non-toxic, relatively cheap and easy to produce in purities greater than 99%. It has been shown by various authors that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds as substitute to conventional corrosion inhibitors that are usually toxic [8-12]. The inhibition effect of three amino acids namely, alanine, glycine and leucine against steel corrosion in HCl solutions has been investigated by potentiodynamic polarization method. The inhibition effect was found to range from 28-91% [13]. The corrosion inhibition of Fe in 1M HCl using twenty two different common amino acids and four related compounds was investigated using potentiodynamic polarization curves [14]. In general, amino acids with longer hydrocarbon chains showed greater inhibition. Additional groups or groups which increased electron density on alpha amino group also increased the inhibition efficiency. The nitrogen containing amino acid L-tryptophan is a derivative of indole.

The molecular structure of the compound suggests that it has strong potential to become an effective corrosion inhibitor. Moretti and Guidi [15] reported the corrosion inhibition of L-tryptophan on copper in aerated 0.5M H$_2$SO$_4$ in the temperature range of 20-50°C. The corrosion rate did not rise as temperature increased. Corrosion inhibition behavior of low carbon steel by L-tryptophan was investigated using weight loss experiment and Tafel polarization curves [16]. The adsorption behavior of L-tryptophan at Fe surface was also investigated by the molecule dynamics simulation method and density functional theory. The results indicated that L-tryptophan could adsorb on Fe surface through the indole ring with π-electrons and nitrogen/oxygen atom with the lone pair electrons in its molecule.

A survey of literature indicates that only limited numbers of references are available dealing with the corrosion inhibition effect of L-tryptophan on mild steel. The present work was undertaken to investigate the corrosion inhibition behavior of L-tryptophan on mild steel in 0.1M HCl solution. The techniques used are weight loss measurements and potentiodynamic polarization measurements.

Fig1. Molecular Structure of L-Tryptophan

MATERIALS AND METHODS

Material preparation

The mild steel specimens having composition (weight %): 0.20 % C, 0.53 % Mn, 0.11 %S, 0.036 % Si and 0.098 % P and
molecular mass 204.23 g mol⁻¹, (CDH, India) was used as received. The stock solutions of 1000 ppm of L-tryptophan in 0.1mol L⁻¹ HCl (MERCK, India) was prepared using double distilled water. The solution was diluted to get inhibitor L-tryptophan solution in the concentration range of 10 ppm to 500 ppm.

**Weight loss measurements**

The mild steel coupons of dimension 2.5 × 2.0 × 0.03 cm were used for weight loss measurements. The coupons were machined and abraded on different grit silicon carbide papers, washed with double distilled water, degreased with absolute ethanol and finally dried in acetone. To hold the specimens a hole of 1.5 mm diameter was made near the edge. The weight loss studies were carried out in the temperature range of 30-50°C. The concentration of L-tryptophan was kept between 10 to 500 ppm in HCl. The weight loss experiments were performed for duration of 6 hrs, as per ASTM designation G1-90. The cleaned mild steel specimens were weighed on a microbalance (Model: Precisa 205A SCS) and suspended in 250 ml beakers containing 200 ml of test solution and placed in a digitally controlled water bath. The temperature of the water bath is controlled by a microprocessor based PID digital temperature indicator-cum-controller with an accuracy of ± 0.5°C. The beakers were kept covered in order to avoid significant water loss. The inhibition efficiency (%IE) was calculated by using the following equation:

\[
\%\text{IE} = \left( \frac{\text{CR}_o - \text{CR}_i}{\text{CR}_o} \right) \times 100
\]

Where, CRᵦ = Corrosion rate of mild steel in blank HCl; CRᵢ = Corrosion rate of mild steel in presence of inhibitor

**Potentiodynamic polarization measurements**

The potentiodynamic polarization measurements were carried out using EG and G potentiostat/Galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG and G: model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and steel coupons as working electrode. The experiments were performed using a scan rate of 0.166 mV/S commencing at a potential above 250mV more active than the stable open circuit potential. All the measurements were carried out at 30°C. Before starting the measurements the specimen were left to attain a steady state which was indicated by a constant potential. The inhibition efficiency was calculated using the relationship:

\[
\text{IE} = \left( 1 - \frac{i_{corr}}{i_{corr}^o} \right) \times 100
\]

Where \(i_{corr}\) = inhibited current density and \(i_{corr}^o\) = uninhibited current density

**RESULTS**

**Weight loss measurements**

The corrosion of mild steel in 0.1M HCl in absence and presence of varying concentration of amino acid L-tryptophan was studied in the temperature range of 30-50°C using weight loss technique. (Table. 1) shows the calculated values of corrosion rate and IE at different concentrations of L-tryptophan under varying temperature. From the data it is clearly seen that the corrosion rate of mild steel depends upon two factors namely, inhibitor concentration and temperature. The corrosion rates are significantly reduced in presence of L-tryptophan. The maximum increase in IE of 64% was observed at a concentration of 500 ppm at 30°C which further increased to 83% on increasing the temperature from 30 to 50°C. The plots of IE as a function of L-tryptophan concentration at 30-50°C (Fig. 2) reveals that IE increases with increase in concentration. Except at very low concentration of L-tryptophan (up to 10 ppm) IE increases with increasing temperature.

<table>
<thead>
<tr>
<th>L-tryptophan (ppm)</th>
<th>Conc.</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition Efficiency (%IE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
<td>50°C</td>
</tr>
<tr>
<td>Blank</td>
<td>102.14</td>
<td>253.62</td>
<td>874.47</td>
</tr>
<tr>
<td>10</td>
<td>57.42</td>
<td>131.32</td>
<td>551.57</td>
</tr>
<tr>
<td>50</td>
<td>55.03</td>
<td>101.46</td>
<td>348.80</td>
</tr>
<tr>
<td>100</td>
<td>47.68</td>
<td>80.25</td>
<td>207.21</td>
</tr>
<tr>
<td>200</td>
<td>46.93</td>
<td>78.79</td>
<td>200.94</td>
</tr>
<tr>
<td>400</td>
<td>42.53</td>
<td>88.46</td>
<td>154.01</td>
</tr>
<tr>
<td>500</td>
<td>36.67</td>
<td>75.52</td>
<td>146.67</td>
</tr>
</tbody>
</table>

![Fig2. Plots of inhibition efficiency (IE) versus inhibitor concentration for mild steel in 0.1M HCl at different temperature of L-tryptophan.](image-url)
The inhibition of mild steel corrosion in presence of various organic compounds have been attributed to their adsorption on the steel surface and are generally confirmed from the fit of the experimental data to various adsorption isotherms. The degree of surface coverage \( \theta \) for various concentrations of L-tryptophan, in 0.1M HCl at 30-50 °C for 6 hrs immersion time has been evaluated by weight loss measurements. The data were tested graphically by fitting to various isotherms and the best result was obtained for Langmuir adsorption isotherm.

According to this isotherm, surface coverage \( \theta \) is related to the inhibitor concentration \( C \) via

\[
\frac{C}{\theta} = \frac{1}{K} + C
\]

where \( \theta \) is the degree of surface coverage, \( K \) is the equilibrium constant of the adsorption process and \( C \) is the L-tryptophan concentration.

Enthalpy of adsorption, \( \Delta H \) and entropy of adsorption, \( \Delta S \) for the corrosion of mild steel in 0.1 M HCl in the presence of L-tryptophan was obtained by the equation:

\[
CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)
\]

\[
\Delta G_{ads} = -RT \ln (55.5 K)
\]

Where \( N \) is the Avogadro's number, \( h \) is the Plank's constant, \( R \) is the molar gas constant and \( T \) is the absolute temperature.

A plot of log \( \theta/1-\theta \) versus 1/T where, \( T \) is the solution temperature was also obtained for L-tryptophan (Fig. 3). The heat of adsorption \( (\Delta Q) \) was calculated from the slope of the plot \((-\Delta H/2.303R)\) and the values are listed in Table 2. The plot of log \( CR/T \) versus 1/T in presence of L-tryptophan (Fig. 4) gave a straight line with slope of \((-\Delta H/2.303R)\) and an intercept of \([\log(R/Nh) + (\Delta S/2.303R)]\). The values of \( \Delta H \) obtained from the slope and \( \Delta S \) evaluated from the intercept are given in Table 2. The value of free energy of adsorption \( (\Delta G_{ads}) \) was calculated using the following equation [17] and the values are listed in Table 3.

Potentiodynamic Polarization Measurements

The potentiodynamic polarization curves for the corrosion of mild steel in 0.1M HCl in absence and presence of varying concentration of L-tryptophan are shown in (fig.5). The values of electrochemical parameters as deduced from these curves e.g., corrosion potential \( (E_{corr}) \) corrosion current density \( (i_{corr}) \), the cathodic tafel slope \( (bc) \), the anodic tafel slope \( (ba) \) and % inhibition efficiency \( (% \text{IE}) \) are shown in Table 4. The IE was calculated using the equation:

\[
% \text{IE} = \left(\frac{i_{corr} - i_{corr}}{i_{corr}}\right) \times 100
\]

Where, \( i_{corr} \) and \( i_{corr} \) are the corrosion current density in absence and presence of inhibitors, respectively.
DISCUSSION

Weight loss measurements

The inhibition behavior of L-tryptophan on mild steel in 0.1 M HCl can be attributed to the adsorption of the molecules on the surface of steel. The effectiveness of the adsorption of L-tryptophan may be attributed to the presence of two nitrogen atoms in the molecule and its large volume [18]. The increased IE with increasing inhibitor concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film [19]. The increase in IE with increasing temperature suggests that at higher concentration L-tryptophan is chemically adsorbed on to the mild steel surface. At lower concentration the adsorbed film is not so stable and gets damaged at higher temperature, thus showing lower IE. The amino acid, L-tryptophan is easily protonated and expected to involve two ways of adsorption. Firstly, it may be adsorbed via donor-acceptor interactions between the π electrons of the indole rings and the unshared electrons pairs of the heteroatom to form a bond with vacant d-orbital of the metal surface [20]. Secondly, the –NH₂ group of amino acid in acid medium is readily protonated and might get adsorbed on the metallic surface via the negatively charged acid anions [21].

The plots of log θ/1-θ versus log C showed a linear correlation of slope close to unity suggesting that adsorption of L-tryptophan on mild steel interface obeys Langmuir adsorption isotherm [16]. The values of heat of adsorption are less than - 40 KJ mol⁻¹ suggesting the physical adsorption of the inhibitors [22]. The negative values of ΔG_ads suggest that the adsorption of L-tryptophan on mild steel is spontaneous. It is an established fact that values of ΔG_ads around -20 KJ mol⁻¹ or less indicates physisorption. The adsorption is attributed to the electrostatic attraction between the charged organic molecules and charged metal surface. The values of ΔG_ads around -40 KJ mol⁻¹ or more are considered as chemisorptions. However, the values of ΔG_ads between -20 and -40 KJ mol⁻¹ gives a disputed Judgment about the type of adsorption [23-26]. In the present investigation the values of ΔG_ads are in the range of -26.70 to -34.85 KJ mol⁻¹ suggesting a mixed type of adsorption involving both physisorption and chemisorption.
Potentiodynamic polarization measurements

The study of electrochemical data reveals that the value of $i_{corr}$ continuously decreases in presence of L-tryptophan. The maximum IE of about 75% was observed at a concentration of 500 ppm indicating that a higher coverage of L-tryptophan on steel surface is obtained in the solution with highest concentration of inhibitor. The values of $E_{corr}$ shifts to more positive value compared to the blank, indicating that L-tryptophan acts more anodic than cathodic inhibitor. The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

Table 4. Potentiodynamic Polarization parameters for corrosion of mild steel in 0.1M HCl in absence and presence of various concentrations of L-tryptophan at 30°C.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ ($\mu$A)</th>
<th>$\beta_c$ (mV)</th>
<th>$\beta_a$ (mV)</th>
<th>C.R (mpy)</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-622.96</td>
<td>666.1</td>
<td>283.19</td>
<td>134.83</td>
<td>58.59</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>-614.41</td>
<td>466.8</td>
<td>263.92</td>
<td>116.64</td>
<td>42.76</td>
<td>29.920</td>
</tr>
<tr>
<td>200</td>
<td>-603.23</td>
<td>435.6</td>
<td>271.522</td>
<td>117.146</td>
<td>39.90</td>
<td>34.60</td>
</tr>
<tr>
<td>500</td>
<td>-573.99</td>
<td>170.1</td>
<td>181.23</td>
<td>121.33</td>
<td>15.59</td>
<td>74.46</td>
</tr>
</tbody>
</table>

Fig 5. Potentiodynamic polarization curves of mild steel in 0.1 M HCl in absence and presence of varying concentration of L-tryptophan (1) Blank (2) 100 ppm (3) 200 ppm (4) 500 ppm.

CONCLUSIONS

1. L-tryptophan showed good performance as corrosion inhibitor for mild steel in 0.1 M HCl.
2. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm. The thermodynamic data suggest mixed type of adsorption involving both physisorption and chemisorption.
3. L-tryptophan acts more anodic than cathodic inhibitor.

ACKNOWLEDGEMENT

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REFERENCES


Inhibition of Mild Steel Corrosion in Acidic Medium Using Starch and Surfactants Additives

M. Mobin, M. A. Khan, M. Parveen

Corrosion Research Laboratory, Department of Applied Chemistry, Aligarh Muslim University, Aligarh 202 002, India

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ABSTRACT: The corrosion inhibition of mild steel in 0.1M H2SO4 in presence of starch (polysaccharide) was studied using weight loss and potentiodynamic polarization measurements in the temperature range of 30–60°C. Starch inhibits the corrosion rates of mild steel to a considerable extent; the maximum inhibition efficiency (%IE) being 66.21% at 30°C in presence of starch concentration of 200 ppm. The effect of the addition of very small concentration of sodium dodecyl sulfate and cetyl trimethyl ammonium bromide on the corrosion inhibition behavior of starch was also studied. The IE of starch significantly improved in presence of both the surfactants. The effect of surfactants on the corrosion inhibition behavior of starch appears to be synergistic in nature. Starch alone and in combination with surfactants is found to obey Langmuir adsorption isotherm from the fit of the experimental data of all concentration and temperature studied. Phenomenon of physical adsorption is proposed from the trend of IE with temperature and also the values E_a, ΔG_ads, and Q_ads obtained. The results obtained by potentiodynamic polarization measurements are consistent with the results of the weight loss measurement. © 2011 Wiley Periodicals, Inc.

Key words: corrosion inhibition; mild steel; polysaccharide; surfactant; adsorption isotherm

INTRODUCTION

The corrosion of iron and steel is a subject of fundamental, academic, and industrial concern and has received a considerable amount of attention. The use of corrosion inhibitors is one of the most practical methods for the protection against corrosion, especially in acid media. The corrosion inhibitors are generally used to protect metals against the attack of the acid solutions, which are widely used in acid pickling, industrial cleaning, acid descaling, and oil-well acidizing, etc. The acid pickling of steel in various industries is generally carried out at temperatures up to 60°C. Corrosion inhibitors are added to the solution during pickling to reduce the degree of metal attack and rate of acid consumption. The inhibitors prevent corrosion either by being adsorbed on the surface of metals or by forming a protective layer, or by causing the formation of insoluble complex. Most of the inhibitors used in industry are organic compounds containing multiple bonds in their molecules that mainly contain nitrogen, sulphur, and/or oxygen atoms through which they get adsorbed on the metal surface. However, most of these substances are toxic and using them is harmful for both human health and environment.

In recent times, a number of polymers have been exploited as corrosion inhibitors due to their inherent stability and cost effectiveness. The functional groups of the polymers form complexes with metal ions, which occupy a large surface area and thus protecting the metals from corrosive agents present in solution. The polymer inhibitors which have been widely examined include: polyethylene glycol, polyvinyl alcohol, polyvinyl pyridine, polyvinyl pyrrolidone, polyethyleneimine, polyacrylic acid, and poly acrylamide. A survey of literature shows that a number of naturally occurring materials such as natural honey, henna, guar gum, opuntia extract, and jojoba oil have shown promising results as corrosion inhibitors for iron and steel in acidic solutions. Recently, inhibition of mild steel corrosion in H2SO4 using synthetic (polyethylene glycol) and naturally occurring (gum arabic) polymer was studied in the temperature range of 30–60°C. Both the polymers were found to act as inhibitors but synthetic polymer was more effective than natural polymer.

Starch is a natural polymer, available in abundance at low cost, renewable, and biodegradable. Chemically it is a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. Starch is produced by all green plants as an energy store. It contains two...
structurally different components namely, amylose (15–20%), and amylopectin (80–85%). The amylose is composed of large linear chain of α (1–4) linked α-D-glucopyanosyl residue, whereas amylopectin is a branching form of α-glycon linked by α (1–6) linkages. The molecular structure of the starch suggests that it has strong potential to become an effective corrosion inhibitor. A survey of literature indicates that only few references are available dealing with the corrosion inhibition effect of starch on aluminum and steel. More recently, modified cassava starches were evaluated as corrosion inhibitor for carbon steel under alkaline conditions in 200 mg/L NaCl solutions. The inhibitive properties were studied by means of electrochemical impedance spectroscopy. The starches were found to show corrosion inhibitive properties; their protection level depended on the type and amount of active groups present in the molecules. Surfactants have been used as corrosion inhibitors either alone or in combination with other compounds to improve their performance as inhibitors. The surfactant molecules possess strong adsorption ability to the metallic surfaces. The adsorb molecules form a monolayer or bilayer hemimicelles or admicelles, depending upon the surfactant concentration and prevent the acid to attack the surface, and thus reduce the corrosion attack. The surfactant can be used either alone or in mixtures with other compounds. The majority of the acidic inhibitors have been known for their specificity of inhibition action. A combination of inhibitors is likely to provide multiple effects required for effective corrosion inhibition. The addition of halide ions to organic compounds has shown synergistic effect and resulted in improved inhibition efficiency (IE) of many organic compounds and reported in the literature. However, the influence of surfactants on the corrosion inhibition behavior of organic compounds is very scanty. This work was undertaken to investigate the inhibition of mild steel corrosion in acidic medium using starch for which no reference is available in the literature. Further, the effect of the addition of very small concentration of sodium dodecyl sulfate (SDS) and cetly trimethyl ammonium bromide (CTAB) on the corrosion inhibition behavior of starch has also been investigated.

EXPERIMENTAL

Material preparation

The mild steel coupons having composition 0.19% C, 0.055% Si, 0.366% Mn, 0.069% P, 0.087% S, 0.074% Ni, 0.075% Cr 0.11% Mo and balance Fe were used for corrosion inhibition studies. The mild steel sheets were mechanically press-cut into coupons of dimension 2.5 × 2 × 0.03 cm. The coupons were machined and abraded on different grades emery papers, washed with double distilled water, degreased with absolute ethanol and finally dried in acetone. A hole of 1 mm dia was made near the edge of the specimen for hooking. The treated coupons were then stored in moisture-free desiccators before their use in corrosion studies. Starch and surfactants SDS and CTAB (MERCK, India) were used as received. The starch selected for the investigation is soluble extra pure having solubility of 50 g/L (90°C), bulk density 300 kg/cm³ and the pH value 6.0–7.5 (20 g/L H₂O₂, 25°C). The concentration of starch prepared and used for the study ranges from 1 to 500 ppm. The concentration of H₂SO₄ prepared and used was 0.1M. All solutions were made using double distilled water. The study was carried out at 30–60°C maintaining the temperatures using a thermostated water bath.

Weight loss measurements

The weight loss experiments were performed for duration of 8 h as per ASTM designation G1–90. The cleaned mild steel coupons were suspended in 250-mL beakers containing 200 mL of test solutions maintained at 30–60°C in a thermostated bath with the aid of glass rods and hooks. The concentration of inhibitor (starch) in H₂SO₄ was kept between 1 and 500 ppm. The weight loss taken was the difference between the weight at a given time and the original weight of the coupons. The measurements were carried out for the uninhibited solution (blank) and solutions containing starch and starch-surfactant mixtures. The corrosion rates were determined using the equation:

\[
\text{Corrosion rate (mpy)} = \frac{534W}{\rho A t} \quad (1)
\]

where, \(W\) is weight loss in mg; \(\rho\) is the density of specimen in g/cm³; \(A\) is the area of specimen in sq. inch and \(t\) is exposure time in hours.

The %IE of starch, surfactants and starch-surfactant mixtures was evaluated using the following equation:

\[
(\%\text{IE}) = \frac{\text{CR}_0 - \text{CR}_i}{\text{CR}_0} \times 100 \quad (2)
\]

where, \(\text{CR}_0\) is the corrosion rate of mild steel in absence of inhibitor and \(\text{CR}_i\) is corrosion rate of mild steel in presence of inhibitor.

Potentiodynamic polarization measurements

Experiments were performed using a conventional three electrode cell assembly, using an EG&G potentiostat/Galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG&G,
model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and mild steel coupons as working electrode. The working electrode was polished with 320, 600, 800 grade emery papers, washed with distilled water, and degreased with acetone. Before starting the measurements, the specimen was left into the solution for 30 min to attain the steady state. The experiments were performed with the potential of $-250$ to $250$ mV at a scan rate of $0.166$ mV/s. All the experiments were carried out at room temperature ($30 \pm 1^\circ$C). The electrochemical experiments data were collected and analyzed by electrochemical software PowrSuit ver. 2.58. The IE was calculated from the measured $i_{\text{corr}}$ values using the relationship:

$$
(\% \text{IE}) = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100
$$

where, $i_{\text{corr}}^0$ is corrosion current density in the absence of inhibitor and $i_{\text{corr}}$ is corrosion current density in the presence of inhibitor.

### RESULTS AND DISCUSSION

#### Weight loss measurements

The corrosion of mild steel in $0.1 \text{M H}_2\text{SO}_4$ in the absence and presence of starch as inhibitor was studied using weight loss technique at temperature range of $30$–$60^\circ$C. The calculated value of corrosion rates and IE for the starch at different concentrations and temperatures is shown in Table I. From the table, it is clearly seen that the corrosion rates are reduced in presence of starch as compared to the free acid solution. Also the corrosion rate increased with increase in temperature at all concentrations. The plot of IE as a function of starch concentrations at $30$–$60^\circ$C (Fig. 1) reveals that IE increases with increase in starch concentration showing a maximum efficiency of $66.21\%$ at $30^\circ$C temperature in presence of starch concentration of $200$ ppm; further addition of starch does not significantly influence the IE. The inhibition of mild steel corrosion in the presence of starch could be attributed to the adsorption of the compound on to mild steel surface, which blocks the metal and thus do not permit the corrosion process to take place. Starch can be adsorbed by the interaction between the lone pair of electrons of the oxygen atom and the steel surface. The presence of $d \pi$ vacant orbital of low energy in the iron atom, as observed in transition group metals, facilitates the adsorption process. In acid, medium starch may be partially hydrolyzed into simpler carbohydrates but the products with higher hydrophilicity than starch is likely to go into the bulk water. As the hydrolysis is quite slow, only negligible starch molecules are expected to hydrolyze and desorbs from the steel surface. Also, the starch in bulk water may occupy the steel surface as the molecules are in dynamic equilibrium. So, even after slow hydrolysis, inhibition by starch is effective.

The increased IE with increasing starch concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film. A decrease in IE with increasing temperature suggests possible desorption

### TABLE I

Calculated Values of Corrosion Rate (mpy) and Inhibition Efficiency (%IE) for Mild Steel in $0.1 \text{M H}_2\text{SO}_4$ in the Absence and the Presence of Starch at $30$–$60^\circ$C from Weight Loss Measurement

<table>
<thead>
<tr>
<th>Starch conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
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<tr>
<td>Blank</td>
<td>200.88</td>
<td>522.74</td>
</tr>
<tr>
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<td>90.99</td>
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<td>5</td>
<td>77.22</td>
<td>227.75</td>
</tr>
<tr>
<td>10</td>
<td>71.28</td>
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<td>69.66</td>
<td>207.64</td>
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<td>68.58</td>
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<td>200.49</td>
</tr>
<tr>
<td>500</td>
<td>70.74</td>
<td>201.39</td>
</tr>
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</table>

**Figure 1** Plot of inhibition efficiency (% IE) against starch concentration for mild steel in $0.1 \text{ M H}_2\text{SO}_4$ at different temperatures.
of some of the adsorbed starch molecules from the metal surface at higher temperatures. This behavior shows that the starch was physically adsorbed on the metal surface.\textsuperscript{34} As the temperature increases, the quantity of equilibrium of adsorption decreases\textsuperscript{35} and as a result, the plot of higher temperatures is below the lower ones. This is clearly demonstrated in Figure 1, which shows that starch is physically adsorbed on the steel surface since the plots of higher temperatures are under that of lower ones. The decrease in IE with increasing temperature may be due to the fact that most of the effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the starch to be adsorbed on the steel surface.

To observe the effect of SDS and CTAB on the corrosion inhibition behavior of starch, the corrosion of mild steel in 0.1\textit{M} H\textsubscript{2}SO\textsubscript{4} in absence and presence of varying concentration of starch with SDS (5 ppm) and CTAB (1 ppm) was separately studied in the temperature range of 30–60\textdegree C by weight loss technique. The results are shown in Tables II and III. It is observed that the corrosion rates of mild steel in 0.1\textit{M} H\textsubscript{2}SO\textsubscript{4} in presence of starch in combination with surfactants is further reduced in comparison to starch alone. Plots of IE versus concentration of starch in combination with surfactants at 30–60\textdegree C are shown in Figures 2 and 3. The anionic SDS binds with starch through electrostatic interaction, thus helps to adsorb at the metal surface more firmly and display higher IE. The IE of starch in presence of 1 ppm of CTAB is also higher than the starch alone. It may be due to the adsorption of starch to the metal surface by binding with CTAB as co-ions or through hydrophobic interaction. The effect of surfactants on the IE of starch in 0.1\textit{M} H\textsubscript{2}SO\textsubscript{4} appears to be synergistic in nature.

### Synergism considerations

The synergism parameter, $S_1$ was evaluated using the relationship:\textsuperscript{36}

$$S_1 = \frac{1 - I_{1+2}}{1 - I_{1}}$$

(4)

where, $I_{1+2} = (I_1 + I_2)$; $I_1$ is IE of starch and $I_2$ is IE of surfactant, SDS/CTAB and $I_{1+2}$ is IE of starch in combination with surfactant. $S_1$ Approaches 1 when

<table>
<thead>
<tr>
<th>Starch conc. (ppm)</th>
<th>SDS conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
<th>Synergism parameter ($S_1$)</th>
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<tr>
<td></td>
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<td>30\degree C</td>
<td>40\degree C</td>
<td>50\degree C</td>
</tr>
<tr>
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<td>Blank</td>
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<td>522.74</td>
<td>1132.70</td>
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<td>409.84</td>
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<tr>
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<td>5</td>
<td>65.46</td>
<td>178.14</td>
<td>421.79</td>
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</table>

### Table III

#### Calculated Values of Corrosion Rate (mpy), Inhibition Efficiency (%IE) and Synergism Parameter ($S_1$) for Mild Steel in 0.1\textit{M} H\textsubscript{2}SO\textsubscript{4} in the Absence and Presence of Varying Concentration of Starch with CTAB at 30–60\textdegree C from Weight Loss Measurement

<table>
<thead>
<tr>
<th>Starch conc. (ppm)</th>
<th>CTAB conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
<th>Synergism parameter ($S_1$)</th>
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</thead>
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<tr>
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<td></td>
<td>30\degree C</td>
<td>40\degree C</td>
<td>50\degree C</td>
</tr>
<tr>
<td>Blank</td>
<td>Blank</td>
<td>200.88</td>
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<td>1132.70</td>
</tr>
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<td>579.43</td>
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<td>62.60</td>
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<tr>
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<td>1</td>
<td>63.91</td>
<td>201.07</td>
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<td>1</td>
<td>67.06</td>
<td>198.81</td>
<td>463.10</td>
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</table>
no interaction between inhibitor (starch) and the surfactant exist, whereas $S_1 > 1$ indicate a synergistic effect. In the case of $S_1 < 1$, antagonistic behavior prevails which may be attributed to competitive adsorption.

The values of the synergism parameter for the various concentrations of starch studied were calculated from the gravimetric data at 30–60°C, and the results are presented in Tables II and III. The synergism parameter $S_1$ is found to be greater than unity indicating that the enhanced IE caused by the addition of surfactants is only due to synergism. The addition of a very small amount of surfactant can improve the adsorption of starch on the mild steel.

**Adsorption considerations**

The adsorption of organic compounds on metal surfaces can be described by two main types of interactions namely, physical adsorption and chemical adsorption. These adsorptions are dependent on the electronic structure of the metal, the nature of the electrolyte and the chemical structure of the organic compounds. The character of adsorption of starch alone and starch in combination with SDS and CTAB was elucidated from the values of degree of surface coverage ($\theta$) calculated from the weight loss data. Attempts were made to fit the $\theta$ values to various adsorption isotherms but best results were obtained for Langmuir adsorption isotherm.

The plots of $C/\theta$ against $C$ are drawn which is characteristics of Langmuir adsorption isotherm given by equation:

$$\frac{C}{\theta} = \frac{1}{K} + C$$  \hspace{1cm} (5)

where $\theta$ is the degree of surface coverage, $K$ is the equilibrium constant of the adsorption process and $C$ is the starch concentration. The plots of $C/\theta$ versus $C$ for mild steel corrosion in 0.1M $\text{H}_2\text{SO}_4$ for starch alone and starch in combination with SDS and CTAB at temperature 30–60°C is shown in Figures 4–6. A linear correlation of slope close to unity suggests that adsorption of starch alone and starch in combination with SDS and CTAB on mild steel
interface obeys Langmuir adsorption isotherm at all the temperatures studied.

**Effect of temperature**

The corrosion of mild steel was studied in the temperature range of 30–60°C in the absence and presence of starch, surfactants and starch in combination with the surfactants. The logarithm of corrosion rate (log CR) versus reciprocal of absolute temperature (1/T) for 0.1 M H₂SO₄ is presented in Figure 7 for blank, starch, surfactants and starch-surfactant mixtures. Linear plot was obtained which indicates that it follows Arrhenius equation given by relationship:

\[
\log \text{CR} = \log A - \frac{E_a}{2.303RT} \tag{6}
\]

where CR is the corrosion rate, A is the Arrhenius constant, \(E_a\) is the apparent activation energy, \(R\) is the molar gas constant and \(T\) is the absolute temperature. The values of \(E_a\) obtained from the slope of the linear plot are presented in Table IV. The increases in \(E_a\) values in presence of the additives compared to the blank indicate the decrease in adsorption process of the inhibitor on the mild steel surface with rise in temperature and a corresponding increase in reaction rate of greater area of metal that is exposed to acid. This shows physical adsorption.

Enthalpy of adsorption, \(\Delta H\) and entropy of adsorption, \(\Delta S\) for the corrosion of mild steel in 0.1 M H₂SO₄ in the presence of starch, surfactants and starch-surfactant mixtures was obtained by the equation:

\[
\text{CR} = \frac{RT}{Nh} \exp \left( \frac{\Delta S}{R} \right) \exp \left( -\frac{\Delta H}{RT} \right) \tag{7}
\]

where \(N\) is the Avogadro’s number, \(h\) is the Planck’s constant, \(R\) is the molar gas constant, and \(T\) is the absolute temperature. Figure 8 shows the plot of log (CR/T) versus 1/T for blank, starch and starch in combination with surfactants. Linear plot was obtained and from the slope (\(-\frac{\Delta H}{RT}\)) and intercept [\(\log \left( \frac{A}{Nh} \right) + \left( \frac{\Delta S}{RT} \right)\)] of the linear plot, the values of \(\Delta H\) and \(\Delta S\), respectively were obtained. The calculated values are presented in Table IV. The enthalpy of adsorption increases in presence of the additives compared to the free acid solution; this indicates physical adsorption. The values of \(\Delta S\) are positive which indicates a decrease in the system order in the presence of additives. Figure 9 shows the plot of log (\(\frac{Q}{100}\)) versus 1/T for starch and starch in combination with the surfactants. Linear plot was obtained and from the slope \(\frac{\Delta G_{\text{ads}}}{RT}\) of the linear plot, heat of adsorption, \(Q_{\text{ads}}\) was obtained. The

**TABLE IV**

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc. 5 ppm</th>
<th>(E_a) (kJ mol(^{-1}))</th>
<th>(\Delta H) (kJ mol(^{-1}))</th>
<th>(\Delta S) (kJ mol(^{-1}) k(^{-1}))</th>
<th>(Q) (kJ mol(^{-1}))</th>
<th>(\Delta G_{\text{ads}}) (kJ mol(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>Blank</td>
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<td>64.98</td>
<td>62.36</td>
<td>5.19</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SDS</td>
<td>5</td>
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<td>27.79</td>
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<tr>
<td>CTAB</td>
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<td>70.19</td>
<td>27.79</td>
<td>–37.74</td>
<td>–32.57</td>
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<tr>
<td>Starch</td>
<td>5</td>
<td>74.50</td>
<td>71.90</td>
<td>28.55</td>
<td>–17.73</td>
<td>–33.54</td>
</tr>
<tr>
<td>Starch + SDS</td>
<td>5 + 5</td>
<td>76.89</td>
<td>74.27</td>
<td>34.68</td>
<td>–19.84</td>
<td>–34.87</td>
</tr>
<tr>
<td>Starch + CTAB</td>
<td>5 + 1</td>
<td>81.85</td>
<td>79.23</td>
<td>50.00</td>
<td>–27.30</td>
<td>–35.54</td>
</tr>
</tbody>
</table>

**Figure 6** Langmuir adsorption isotherm for (starch + 1 ppm CTAB) adsorbed on mild steel surface in 0.1 M H₂SO₄ at different temperatures.

**Figure 7** Adsorption isotherm plot for log CR versus 1/T in the absence and presence of starch, SDS, CTAB, and starch in combination with SDS/CTAB.
calculated values of $Q_{ads}$ were negative (Table IV) indicating that the adsorption of starch, SDS, CTAB, and starch-surfactant mixture on mild steel surface is exothermic.\textsuperscript{41} In general, the values are less than $-40$ kJ mol$^{-1}$ suggesting the physical adsorption of the compounds.\textsuperscript{42}

Free energy of adsorption, $\Delta G_{ads}$ was obtained from the intercept of plot of log (% IE) versus log inhibitor concentration (log C) and evaluated using the following equation.

$$\log C = \log \left( \frac{\theta}{1-\theta} \right) - \log B$$  \hspace{1cm} (8)

where, $\log B = -1.74 - \left( \frac{\Delta G_{ads}}{2.303RT} \right)$ and $C_i$ is the concentration of the system studied. The calculated values of $\Delta G_{ads}$ from 30 to 60°C for the various systems studied are presented in Table IV. The $\Delta G_{ads}$ values obtained are negative, which indicate the spontaneous adsorption of the starch and starch in combination with surfactants on the mild steel surface. The value of $\Delta G_{ads}$ of $-40$ kJ/mol is usually accepted as a threshold value between chemisorptions and physisorption. The values of $\Delta G_{ads}$ obtained in this study are below $-40$ kJ/mol (between $-9.96$ and $-35.54$ kJ/mol). This

Potentiodynamic polarization measurements

The potentiodynamic polarization curves for the corrosion of mild steel in 0.1 M H$_2$SO$_4$ in absence and presence of varying concentration of starch and starch in combination with 5 ppm of SDS and 1 ppm of CTAB are shown in Figures 10 and 11. The values of electrochemical parameters as deduced from these curves, e.g., corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), the anodic tafel slope ($b_a$), the cathodic tafel slope ($b_c$), corrosion rate and % IE are shown in Table V.

The study of electrochemical data (Table V) reveals that the value of $i_{corr}$ continuously decreases in
presence of starch. The maximum IE of about 61.75% was observed at a concentration of 200 ppm indicating that a higher coverage of starch on steel surface is obtained in the solution with highest concentration of inhibitor. The values of $E_{corr}$ shifts to more positive value compared to the blank, indicating that starch acts more anodic than cathodic inhibitor. The addition of 5 ppm of SDS to varying concentration of starch improved the IE of starch significantly. However, the effect of SDS is more pronounced at lower concentrations of starch. The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

**CONCLUSIONS**

1. Starch showed good performance as corrosion inhibitor for mild steel in 0.1M $\text{H}_2\text{SO}_4$ which is further improved in presence of surfactants SDS and CTAB. The effect of surfactants on corrosion inhibition behavior of starch appears to be synergistic in nature. Phenomenon of physical adsorption is proposed from the trend of IE with temperature.

2. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm at all the concentrations and temperatures studied.

3. The results of potentiodynamic polarization measurements show that starch acts more anodic than cathodic inhibitor. The results are consistent with the results of the weight loss measurements.

**References**

42. Jha, L. J. Ph.D. Thesis, Faculty of Science, Delhi University, Delhi, 1990.

**TABLE V**

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc. (ppm)</th>
<th>$E_{corr}$ (mv)</th>
<th>$I_{corr}$ (µA)</th>
<th>$BET$ (m²/g)</th>
<th>$σc$ (mv)</th>
<th>CR (mpy)</th>
<th>(%IE)</th>
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<td>5</td>
<td>–589.965</td>
<td>3458.00</td>
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<td>237.081</td>
<td>319.70</td>
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Inhibition of Mild Steel Corrosion Using l-Histidine and Synergistic Surfactants Additives

M. Mobin, Mosarrat Parveen & M. Z. A. Rafiquee
Inhibition of Mild Steel Corrosion Using L-Histidine and Synergistic Surfactants Additives

M. Mobin, Mosarrat Parveen, and M.Z.A. Rafiquee

(Submitted January 25, 2012; in revised form May 5, 2012)

The corrosion inhibition behavior of nitrogen-containing amino acid L-Histidine (LHS) on mild steel in 0.1 M H₂SO₄ solution in the temperature range of 30-60 °C was studied by weight loss measurements, and potentiodynamic polarization measurements. The effect of the addition of very small concentration of surfactants, sodium dodecyl sulfate (SDS), and cetyltrimethyl ammonium bromide (CTAB), respectively on the corrosion inhibition behavior of LHS was also studied. The surface morphology of the corroded steel samples was evaluated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). LHS significantly reduces the corrosion rates of mild steel, with the maximum inhibition efficiency (IE) being 71.09% at 30 °C in the presence of 500 ppm of LHS. The IE of LHS is synergistically increased in the presence of SDS and CTAB. The SEM and AFM photographs show a clearly different surface morphology in the presence of additives. LHS alone and in combination with surfactants obeys Langmuir adsorption isotherm from the fit of the experimental data of all concentration and temperature studied. The calculated thermodynamic parameters for adsorption reveal strong interaction between the inhibitors and the mild steel surface, and suggest physical adsorption. The results obtained by potentiodynamic polarization measurements are consistent with the results of the weight loss measurement. LHS acts more anodic than cathodic inhibitor.

Keywords AFM, corrosion inhibitor, L-histidine, mild steel, potentiodynamic polarization, SEM, surfactants

1. Introduction

Among the metals, mild steel is the most extensively investigated metals for corrosion studies because of its wide application in different corrosive environments. It is subjected to excessive corrosion attack when exposed to service in aqueous acidic environments (Ref 1, 2). One of the important and practical methods of protecting steel from corrosion is the use of inhibitors (Ref 3-5). A number of organic compounds containing heteroatoms such as N, O, S and P in their aromatic ring or long carbon chain have been widely used as potential corrosion inhibitor in acid solutions (Ref 6, 7). These compounds prevent corrosion by blocking the active corrosion sites either by getting adsorbed, or by forming a protective layer or an insoluble complex on the metal surface. The inhibitive action of these compounds depends on the structure of molecule, corrosion environment, the charge and nature of metal surface and organic molecule (Ref 8-12). However, most of the organic compounds used as inhibitor are synthetic chemicals, expensive, and very hazardous to both human beings and the environments and need to be replaced with nontoxic and environmental friendly compounds.

In order to promote green chemistry, electrochemists and corrosion engineers have been looking for naturally occurring organic substances or biodegradable organic materials that can be used as metal corrosion inhibitors. Amino acids represent a category of organic compounds, which fulfills many of the aspects needed for such purpose. They are naturally occurring, relatively cheap, and their structure and properties are long established (Ref 13). They contain carboxyl and amino functionalities bonded to the same carbon atom and are nontoxic, completely soluble in aqueous media and are easy to produce in purities greater than 99%. It has been shown that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds as substitute to conventional corrosion inhibitors that are usually toxic (Ref 14-22). The nitrogen-containing amino acid LHS is a derivative of imidazole. The molecular structure of the compound (Fig. 1) suggests that it has strong potential to become an effective corrosion inhibitor. This may be due to the presence of the highly donating imidazole group which can increase the charge density on the adsorbed sites of the molecule. It is important to mention that imidazole-containing compounds are often used as corrosion inhibitors and as adhesion promoters particularly on copper (Ref 23, 24).

Synergism is one of the most important effects in inhibition process and serves as the basis for most of the modern corrosion-inhibiting formulations. The addition of halide ions to organic compounds has shown synergistic effect and resulted in improved IE of many organic compounds (Ref 25). The IE of amino acid methionine was also found to be synergistically increased in the presence of KI (Ref 26). However, there remain relatively few studies directed toward the synergistic between the different organic compounds and surfactants (Ref 27, Ref 28). The influence of surfactants SDS, CTAB, and TX-100 on the corrosion inhibition behavior of
2-amino-3-(4-imidazolyl) propanoic acid, molecular mass 155.15 g/mol, SDS, and CTAB (CDH, India) were used as received. The stock solution of LHS was prepared in 0.1 mol/L H₂SO₄ and desired concentrations were obtained by appropriate dilutions. The concentration of inhibitor used for the study ranges from 10 to 1000 mg/L. All the solutions were prepared using double-distilled water. The study was carried out at “(30-60) °C” maintaining the temperature using a thermostated water bath.

2.2 Weight Loss Measurements

The freshly prepared mild steel coupons were suspended in 250-mL beakers containing 200 mL of test solution maintained at “(30-60) °C” in a thermostated water bath with the aid of glass rods and hooks. The weight loss taken was the difference between the weight at a given time and the original weight of the coupons. The measurements were carried out for the uninhibited solution and the solution containing LHS and LHS-surfactant mixtures. Weight loss experiments were performed for duration of 6 h, as per ASTM designation G1-90. The corrosion rates were determined using the equation:

\[
\text{Corrosion rate (mpy)} = \frac{534W}{\rho At}
\]

where, \( W \) is the weight loss in mg; \( \rho \) is the density of the specimen in g/cm², \( A \) is the area of specimens in sq.in, and \( t \) is the exposure time in hours.

The IE of LHS, surfactants and LHS-surfactant mixture was calculated using the following equation:

\[
\% \text{IE} = \left( \frac{CR_o - CR_i}{CR_o} \right) \times 100,
\]

where \( CR_o \) is the corrosion rate of mild steel in the absence of inhibitor; and \( CR_i \) is the corrosion rate of mild steel in the presence of inhibitor.

2.3 Potentiodynamic Polarization Measurements

The potentiodynamic polarization measurements were carried out using potentiostat/Galvanostat, model: PGSTAT30 controlled by a PC through the general purpose electrochemical system (GPES) software provided by AUTOLAB. The experiments were carried out in a standard three-electrode cell of Ag/AgCl electrode (saturated KCl) as reference electrode, Pt. wire as counter electrode and steel coupons as working electrode. The experiments were performed using a scan rate of 0.5 mV/S commencing at a potential above 250 mV more active than the stable open circuit potential. All the measurements were carried out at room temperature (30 ± 1 °C). Before starting the measurements, the specimen were left in the solution for 30 minutes to attain a steady state which was indicated by a constant potential. The IE was calculated using the relationship:

\[
\text{IE(%) = } \left( 1 - \frac{i_{corr}}{i_{corr}^0} \right) \times 100.
\]

where \( i_{corr} \) = inhibited current density, and \( i_{corr}^0 \) = uninhibited current density.

2.4 SEM and AFM Studies

SEM model: 430 LEO electron microscopy Ltd Cambridge, England; and AFM model: Innova SPM, Veeco were used to study the morphology of the corroded steel surface in the presence and the absence of the inhibitors. To study the surface morphology of mild steel, polished specimens before initiation of any corrosion reaction, were examined in optical microscope to find out any surface defects, such as pit or noticeable irregularities like cracks etc. Only those specimens, which had a smooth pit-free surface, were subjected to immersion. After completion of the tests, the specimens were thoroughly washed with double-distilled water, dried, and then subjected to SEM and AFM examination.
3. Results and Discussion

3.1 Weight Loss Measurements

The corrosion of mild steel in 0.1 M H$_2$SO$_4$ in the absence and the presence of varying concentrations of LHS alone and in combination with surfactants SDS and CTAB was studied in the temperature range of “(30-60) °C” using weight loss technique. The data obtained after 6 h of immersion are presented in Fig. 2, 3, and 4. The corrosion rate of mild steel is reduced in the presence of LHS as compared to free acid solution and depends upon inhibitor concentration and temperature. The IE increases with increasing LHS concentration showing a maximum increase in IE of 71.09% at 500 ppm at 30 °C (Fig. 2). The increased IE with increasing inhibitor concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film (Ref 35). The further increase in LHS concentration causes slight decrease in IE possibly due to the dissolution of adsorbed inhibitor film (Ref 36). Also a decrease in IE is observed with increase in temperature at all the concentrations studied. This suggests that physical adsorption as the weak Vander Waal’s forces responsible for such type of interaction tends to disappear at elevated temperatures.

The inhibition behavior of LHS on mild steel in 0.1 M H$_2$SO$_4$ can be explained in terms of the adsorption of its molecules on the surface of steel. The effectiveness of the adsorption may be attributed to the presence of two nitrogen (one in imidazole ring and other in the amino group) and oxygen atom (carbonyl group) in the molecule and its large volume. Further, amino group is easily protonated in the acidic medium, so it could be electrostatically attracted to the cathodic sites on steel surface. The oxygen atom carrying two lone pair of electrons could be adsorbed on the anodic site of steel surface (Ref 37). Therefore, LHS is expected to involve two ways of adsorption. When the surface of steel is saturated with the inhibitor, LHS, the further increase in LHS concentration causes desorption from the steel surface due to association of protonated LHS molecules in acidic medium. The inhibitor LHS exists in the protonated form in the presence of H$_2$SO$_4$ and at higher concentrations association among the LHS molecules occurs via intermolecular H-bonding. The intermolecular H-bonding between the protonated molecules leads to dimer formation and results in the dissolution of adsorbed LHS molecules. Thus, the molecular associations among LHS cause desorption of adsorbed molecules and increase the concentration in the bulk solution, thereby, causing decrease in the IE values. To observe the effects of SDS and CTAB on the corrosion inhibition behavior of LHS, the corrosion behaviors of mild steel in 0.1 M H$_2$SO$_4$ in the absence and the presence of varying concentrations of LHS in combination with 5 ppm of SDS and 1 ppm of CTAB were separately studied in the temperature range of “(30-60) °C”. Figures 3 and 4 show the plots of IE as a function of varying concentrations of LHS in combination with 5 ppm of SDS and 1 ppm of CTAB, respectively at “(30-60) °C”. The SDS and CTAB also exhibit corrosion inhibition of mild steel in 0.1 M H$_2$SO$_4$. The corrosion rates of mild steel in the presence of LHS in combination with surfactants is further reduced in comparison with LHS alone. It is observed that the mixture of LHS and SDS or LHS and CTAB increases the IE more than either LHS or surfactants alone, indicating a synergistic effect between LHS and surfactants. The mixed LHS and CTAB is more effective as an inhibitor for steel corrosion than that the mixture of LHS and SDS. Considering the effect of surfactants on the corrosion inhibition behavior of LHS, the surfactant molecules help the LHS molecules to adhere to the steel surface more firmly. The forces of interactions which are responsible for the
adherence of LHS to the steel surface are; imidazole ringhydrocarbon chain (of both the SDS and CTAB), positively charged amino -NH$_3^+$-DS$^-$ headgroup and –COO$^-$ (of LHS) – CTA$^+$ (headgroup of CTAB). In addition, the surfactant molecules also adhere to the steel surface unoccupied by the LHS molecules. The effect of surfactants on the IE of LHS in 0.1 M H$_2$SO$_4$ appears to be synergistic in nature.

3.2 Synergism Considerations

The interaction of LHS and surfactants SDS/CTAB can be described by synergism parameter $S_1$ (Ref 38) which is defined as

$$S_1 = \frac{1 - I_1}{1 - I_{1+2}}$$  \hspace{1cm} (Eq 4)

where, $I_{1+2} = (I_1 + I_2)$; $I_1$ is the IE of LHS, and $I_2$ is the IE of surfactants, SDS/CTAB, and $I'_{1+2}$ being IEs of LHS in combination with surfactants. $S_1$ approaches 1 when no interaction between the inhibitor molecules exists while $S_1 > 1$ indicates a synergistic effect. In the case of $S_1 < 1$, antagonistic behavior prevails which may be attributed to competitive adsorption.

The values of synergism parameter for the various concentration of LHS studied were calculated from the gravimetric data at “(30-60) °C”, and the results are given in Table 1. The values are all greater than unity. This is an indication that the enhanced IE resulting from the addition of surfactants to LHS is synergistic in nature and proves that the addition of a very small concentration of surfactants can significantly improve the adsorption of LHS on the mild steel surface.

3.3 Adsorption Isotherms

The inhibition of mild steel corrosion in the presence of various organic compounds have been attributed to their adsorption on the steel surface and are generally confirmed from the fit of the experimental data to various adsorption isotherms. The degree of surface coverage ($\theta$) for various concentrations of LHS, and LHS in combination with surfactants have been used to explain the best isotherm to determine the adsorption process. The data were tested graphically by fitting to various isotherms, and the best result was obtained for Langmuir adsorption isotherm. The plots of $C/\theta$ against $C$ are drawn which are the characteristics of Langmuir adsorption isotherm given by the equation:

$$C = \frac{1}{\theta} = \frac{k}{C} + C$$  \hspace{1cm} (Eq 5)

where $\theta$ is the degree of surface coverage, $C$ is the inhibitor concentration, and $k$ is the equilibrium constants of adsorption.

The plots of $C/\theta$ against $C$ gave a straight line for mild steel in 0.1 M H$_2$SO$_4$ in the presence of LHS alone and in combination with surfactants (Fig. 5, 6, 7). A linear correlation of slope close to unity suggest that adsorption of LHS alone and in combination with surfactants on mild steel interface obeys Langmuir adsorption isotherm at all the temperature studied.

3.4 Effect of Temperature

The dependences of logarithm of corrosion rate ($\log CR$) on the reciprocal of absolute temperature ($1/T$) for 0.1 M H$_2$SO$_4$ for blank, and LHS alone and in combination with SDS and CTAB, are presented in Fig. 8. Linear plots were obtained which indicates that it follows Arrhenius equation:

$$\log CR = \log A - \frac{E_a}{2.303 RT}$$  \hspace{1cm} (Eq 6)

where $CR$ is the corrosion rate, $A$ is the Arrhenius constant, $E_a$ is the apparent activation energy, $R$ is the molar gas constant, and $T$ is the absolute temperature.

The activation energy ($E_a$) values obtained from the slope of the linear plots are shown in Table 2. The values were higher in the presence of the additive compared to the blank. The higher value of $E_a$ in the presence of the additive and the decrease in the % IE with rise in temperature are interpreted as an

### Table 1 Calculated values of synergism parameter ($S_1$) for mild steel in 0.1 M H$_2$SO$_4$ in the absence and the presence of LHS and surfactants SDS/CTAB at 30-60 °C from weight loss measurement

<table>
<thead>
<tr>
<th>Inhibitor conc., ppm</th>
<th>Surfactant conc., ppm</th>
<th>30 °C</th>
<th>40 °C</th>
<th>50 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>SDS</td>
<td>1.18</td>
<td>1.14</td>
<td>1.36</td>
<td>1.39</td>
</tr>
<tr>
<td>50</td>
<td>SDS</td>
<td>1.18</td>
<td>1.27</td>
<td>1.34</td>
<td>1.33</td>
</tr>
<tr>
<td>100</td>
<td>SDS</td>
<td>1.23</td>
<td>1.31</td>
<td>1.09</td>
<td>0.91</td>
</tr>
<tr>
<td>200</td>
<td>SDS</td>
<td>1.19</td>
<td>1.17</td>
<td>1.08</td>
<td>1.01</td>
</tr>
<tr>
<td>300</td>
<td>SDS</td>
<td>1.16</td>
<td>1.12</td>
<td>1.08</td>
<td>1.02</td>
</tr>
<tr>
<td>500</td>
<td>SDS</td>
<td>1.19</td>
<td>1.19</td>
<td>1.07</td>
<td>1.15</td>
</tr>
<tr>
<td>700</td>
<td>SDS</td>
<td>1.18</td>
<td>1.18</td>
<td>1.08</td>
<td>1.19</td>
</tr>
<tr>
<td>1000</td>
<td>SDS</td>
<td>1.28</td>
<td>1.18</td>
<td>1.15</td>
<td>1.19</td>
</tr>
<tr>
<td>10</td>
<td>CTAB</td>
<td>1.42</td>
<td>1.33</td>
<td>1.55</td>
<td>1.61</td>
</tr>
<tr>
<td>50</td>
<td>CTAB</td>
<td>1.44</td>
<td>1.46</td>
<td>1.63</td>
<td>1.46</td>
</tr>
<tr>
<td>100</td>
<td>CTAB</td>
<td>1.49</td>
<td>1.39</td>
<td>1.41</td>
<td>1.13</td>
</tr>
<tr>
<td>200</td>
<td>CTAB</td>
<td>1.54</td>
<td>1.36</td>
<td>1.36</td>
<td>1.03</td>
</tr>
<tr>
<td>300</td>
<td>CTAB</td>
<td>1.51</td>
<td>1.36</td>
<td>1.36</td>
<td>0.94</td>
</tr>
<tr>
<td>500</td>
<td>CTAB</td>
<td>1.57</td>
<td>1.45</td>
<td>1.35</td>
<td>1.14</td>
</tr>
<tr>
<td>700</td>
<td>CTAB</td>
<td>1.59</td>
<td>1.44</td>
<td>1.44</td>
<td>1.05</td>
</tr>
<tr>
<td>1000</td>
<td>CTAB</td>
<td>1.67</td>
<td>1.45</td>
<td>1.46</td>
<td>1.21</td>
</tr>
</tbody>
</table>
indication of physiosorption (Ref 39-41). Enthalpy of adsorption, $D_H$ and entropy of adsorption, $D_S$ for the corrosion of mild steel in 0.1 M H$_2$SO$_4$ in the presence of LHS alone and in combination with surfactants were obtained by the following equation:

$$CR = \frac{RT}{Nh} \exp \left( \frac{\Delta S}{R} \right) \exp \left( - \frac{\Delta H}{RT} \right)$$  \hspace{1cm} (Eq 7)

where $N$ is the Avogadro’s number, $h$ is Plank’s constant, $R$ is the molar gas constant, and $T$ is the absolute temperature. Figure 9 shows the plot of log ($CR/T$) against $1/T$ for blank, LHS alone and in combination with surfactants. From the slope ($-\Delta H/2.303R$) and intercept ($[\log(R/Nh) + (\Delta S/2.303R)]$) of the linear plots, $\Delta H$ and $\Delta S$, respectively were obtained. The calculated values are shown in Table 2.

$$\Delta G_{ads} = -RT\ln(55.5K),$$  \hspace{1cm} (Eq 8)

where $K$ is the equilibrium constant and is given by

$$K = \frac{\theta}{C(1-\theta)},$$  \hspace{1cm} (Eq 9)

where $\theta$ is the degree of surface coverage, $C$ the concentration of inhibitors in mol/dm$^3$, $R$ is the gas constant, and $T$ is the solution temperature. The calculated values of $\Delta G_{ads}$ from 30 to 60 °C for the various systems studied are presented in Table 2. The negative values of $\Delta G_{ads}$ indicate the stability of the adsorbed inhibitor on the mild steel surface and the spontaneity of the process. An increase in $\Delta G_{ads}$ (becomes less negative) with increase in temperature suggests the occurrence of exothermic process. It is an established fact that values of $\Delta G_{ads}$ $\approx$ 20 kJ/mol or less indicates physiosorption. The adsorption is attributed to the electrostatic attraction between the charged organic molecules and charged metal surface. The values of $\Delta G_{ads}$ around $-40$ kJ/mol or more are indicative of charge sharing or transferring from organic species to the metal surface to form a coordinate type of metal bond (i.e. chemisorptions). The values of $\Delta G_{ads}$ obtained in this study are below $-40$ kJ/mol (between $-13.09$ and $-29.27$ kJ/mol). This is consistent with electrostatic interaction between the charged molecules and the charge metals, which is indicative of physical adsorption.
3.5 Potentiodynamic Polarization Measurements

The potentiodynamic polarization curves for the corrosion of mild steel in 0.1 M H₂SO₄ in the absence and the presence of LHS, SDS, CTAB, and LHS in combination with SDS/CTAB are shown in Fig. 10. The values of electrochemical parameters as deduced from these curves, e.g., the corrosion potential (E_{corr}), the corrosion current density (i_{corr}), the cathodic Tafel slope (b_c), the anodic Tafel slope (b_a), and % IE are shown in Table 3. The IE was calculated using the equation:

\[
\%IE = \left( \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \right) \times 100
\]  

(Eq 10)

where \(i_{corr}^0\) and \(i_{corr}\) are the corrosion current density in the absence and the presence of inhibitors, respectively. The study of electrochemical data reveals that the value of \(i_{corr}\) decreases in the presence of additives. The values of \(E_{corr}\) in the presence of LHS, surfactants, and LHS-surfactant mixture shift to more positive values compared with the blank, indicating that the compounds act more anodic than cathodic as inhibitors. The positive shift in \(E_{corr}\) is more pronounced in the presence of LHS-surfactant mixture, suggesting the dominant role of anodic suppression in the process (Ref 44). The values obtained from weight loss and electrochemical methods remain different; this may be because IE calculated from weight loss method is an average value, while the IE obtained from electrochemical method in an instantaneous value rather than an average value. The electrochemical results on the whole are in good agreement with the weight loss results.

3.6 Surface Morphological Studies

Surface photographs were obtained by means of SEM and AFM so as to determine if the mild steel corrosion inhibition is

![Fig. 9](image-url) Adsorption isotherm plots for log CR/T vs. 1/T in the absence and the presence of LHS, SDS, CTAB, and LHS in combination with SDS/CTAB

![Fig. 10](image-url) Potentiodynamic curves for mild steel in 0.1 M H₂SO₄ in the absence and the presence of various concentrations of additives (a) Blank, (b) SDS 5 ppm, (c) LHS 200 ppm, (d) LHS 200 ppm + SDS 5 ppm, and (e) LHS 200 ppm + CTAB 1 ppm

### Table 2 Calculated values of kinetic/thermodynamic parameters for mild steel in 0.1 M H₂SO₄ in the absence and the presence of LHS and LHS-surfactants SDS/CTAB mixtures from weight loss measurement

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc., ppm</th>
<th>(E_a), kJ/mol</th>
<th>(\Delta H), kJ/mol</th>
<th>(\Delta S), kJ/mol/k</th>
<th>(\Delta G_{ads}), kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td>46.39</td>
<td>43.25</td>
<td></td>
<td>(\ldots)</td>
</tr>
<tr>
<td>LHS 200</td>
<td></td>
<td>67.95</td>
<td>63.34</td>
<td>10.42</td>
<td>-15.97</td>
</tr>
<tr>
<td>SDS 5</td>
<td></td>
<td>55.31</td>
<td>52.00</td>
<td>20.65</td>
<td>-21.59</td>
</tr>
<tr>
<td>CTAB 1</td>
<td></td>
<td>73.85</td>
<td>68.89</td>
<td>29.64</td>
<td>-29.27</td>
</tr>
<tr>
<td>LHS + SDS</td>
<td>200 + 5</td>
<td>84.36</td>
<td>78.56</td>
<td>55.49</td>
<td>-18.23</td>
</tr>
<tr>
<td>LHS + CTAB</td>
<td>200 + 1</td>
<td>89.56</td>
<td>84.49</td>
<td>72.88</td>
<td>-19.02</td>
</tr>
</tbody>
</table>

### Table 3 Potentiodynamic polarization parameters for corrosion of mild steel in 0.1 M H₂SO₄ in the absence and the presence of various concentrations of LHS and LHS-surfactants SDS/CTAB mixtures at 30 °C

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc., ppm</th>
<th>(E_{corr}), mV</th>
<th>(i_{corr}), A/cm²</th>
<th>(b_a), mV/dec</th>
<th>(b_c), mV/dec</th>
<th>(CR), mmpy</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td>-507</td>
<td>3.398 \times 10^{-4}</td>
<td>214</td>
<td>314</td>
<td>3.951</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>LHS 200</td>
<td></td>
<td>-471</td>
<td>8.483 \times 10^{-5}</td>
<td>175</td>
<td>235</td>
<td>0.986</td>
<td>75.03</td>
</tr>
<tr>
<td>SDS 5</td>
<td></td>
<td>-490</td>
<td>2.455 \times 10^{-4}</td>
<td>50</td>
<td>219</td>
<td>2.854</td>
<td>27.75</td>
</tr>
<tr>
<td>CTAB 1</td>
<td></td>
<td>-489</td>
<td>9.770 \times 10^{-5}</td>
<td>152</td>
<td>117</td>
<td>1.136</td>
<td>71.25</td>
</tr>
<tr>
<td>LHS + SDS</td>
<td>200 + 5</td>
<td>-469</td>
<td>4.080 \times 10^{-5}</td>
<td>64</td>
<td>183</td>
<td>0.474</td>
<td>87.99</td>
</tr>
<tr>
<td>LHS + CTAB</td>
<td>200 + 1</td>
<td>-459</td>
<td>3.331 \times 10^{-5}</td>
<td>62</td>
<td>204</td>
<td>0.387</td>
<td>90.79</td>
</tr>
</tbody>
</table>
due to the formation of a protective film by adsorption of inhibitors. Considering the results of the SEM studies on steel before its immersion in the solutions, except the presence of polishing scratches, the surface shows the absence of noticeable defects such as pits and cracks (Fig. 11). In uninhibited acid solution, a damaged and heterogeneous surface is observed (Fig. 12). The surface heterogeneity is considerably decreased in the presence of LHS-inhibited acid solution which is further decreased in the presence of surfactant additives (Fig. 13, 14, 15). The SEM results are further proved by AFM photographs of steel specimens taken in the absence and the presence of inhibitors at room temperature in the range of 0-1 and 0-2 μm, respectively. In the absence of inhibitor, the AFM photograph (Fig. 16) clearly shows the presence of grooves with higher values (peaks of the order of μm), whereas in the presence of inhibitor, a comparatively smoother surface (peaks of the order of nm) is observed (Fig. 17). A smoother layer with a clearly different morphology is a result of the formation of a protective layer by the adsorbed inhibitor. The inhibitor layer is not very
compact, and as such does not provide absolute coverage, with some metal sites being still exposed to acid attack.

4. Conclusions

1. L-histidine (LHS) showed good performance as corrosion inhibitor for mild steel in 0.1 M H$_2$SO$_4$ which is further improved in the presence of surfactants SDS and CTAB. The effect of surfactants on corrosion inhibition behavior of LHS appears to be synergistic in nature.

2. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well to the Langmuir adsorption isotherms at all the concentrations and temperatures studied. The values of free energy of adsorption indicate stability of the adsorbed inhibitor on the mild steel surface and confirm the spontaneity of the process and its physical nature.

3. LHS acts more anodic than cathodic as inhibitor.

4. SEM and AFM studies further confirm the inhibitive character of the additives.

References


5. C.C. Nathan, Organic Inhibitor, NACE, Houston, TX, 1977, p 11–20


