ABSTRACT

The inhibition of mild steel (MS) in 1 M HCl solution with aqueous extract of Ziziphus Jujuba roots (AEZJR) was studied by weight loss method at 303-333K temperatures. It was found that inhibition efficiency increased with increase in concentration of extract and decreased with increase in temperature. Maximum 62.68% inhibition efficiency was observed at 303 K and at 8% (v/v) concentration of extract. Adsorption of extract at mild steel surface follows Langmuir adsorption isotherm. Physorption is proposed by the values of Gibbs free energy, variation in inhibition energy with temperature and with activation energy values trend. Negative values of Gibbs energy reveals the spontaneity of inhibition process in extract at studied temperatures.


1. INTRODUCTION

Mild steel is generally used in structural industries. It is also used in transport and mechanical industries. Although it is common metal alloys to use in various industries but it have a major problem which is corrosion. Corrosion is the degradation of metal and their alloys by an electrochemical reaction and environment. The introduction of corrosion inhibitors is the best way to prevent metallic corrosion and save the great economic loss of country (48, 49)

Generally many chemical compounds is used for corrosion inhibitors but they are toxic and expansive. Green inhibitors are generally extracts of various part of plant. Which is eco friendly non toxic and low cost. They have great corrosion inhibitor property. So they are widely used as corrosion inhibitors for metal and its alloys in acidic, basic and neutral medium.

Literature survey reveals various plant extracts that have been used as corrosion inhibitors for protection of different metals and their alloys. Extract of fenugreek seeds and roots[18], essential oils of Menthaspicata, Lavandul amultifida, Pulicari amauritanica [6,37,38] Azadirachta indica[24,27], extract of Ananascomosus L.[9], Embilicaofficinalis[26], Garcinacola and Cola nitida[8], Nerium olender leaves [48], Calotropis procera [49] etc. have been studied. In the continuity of above corrosion inhibition studies, the present work reveals the adsorption behavior and corrosion prevention properties of aqueous extract of roots of Ziziphus Jujuba for mild steel in 1 M HCl solution.

2. MATERIALS AND METHODS

Preparation of extract

The roots of Ziziphus Jujuba plant were taken, washed and air dried for 6-7 days, crushed and grind mechanically. 20 g of ground roots were heated in 200 ml distill water for one hour using air condenser at 70⁰C - 80⁰C. This extract was left overnight and then filtered and make up to 200 ml with distill water for the experiment.

Selection of steel specimens

Rectangular mild steel specimens of 5 cm length and 1 cm width were taken and abraded with a series of emery papers, degreased with acetone, washed with distill water, dried and constant weight was recorded by electronic balance.
Solution Preparation

1M HCl solution was prepared by 37% HCl (Merk Ltd.) using distill water. The employed concentration range of aqueous extract of *Ziziphus Jujuba* roots (AEZJR) was 1% to 8% (v/v).

Gravimetric Measurement

Gravimetric method is widely used method because of its reliability and simplicity in corrosion inhibition experiments. For each experiment 100 ml test solutions were taken in 250 ml beaker and Rectangular specimen was immersed in it with plastic thread for one hour. The experiments were carried out at different temperatures ranges from 303 K to 333K in thermostatic water bath. After one hour specimens were removed, washed with distill water, acetone dried and abraded with series of emery papers and then weighted accurately with electronic balance. It was noted that the surfaces of specimens became more rough in test solutions without the inhibitor than the surfaces of specimens which were immersed in test solutions containing different concentrations of inhibitor.

3. RESULT AND DISCUSSION

3.1 Corrosion rates

Corrosion rates were calculated by following equation (1).[1, 34]

\[
C R \ (g \ cm^{-2} \ min^{-1}) = \frac{(W_1-W_2)}{At}
\]  

(1)

Where CR is corrosion rate, W1 is weight of mild steel specimen without inhibitor and W2 is weight loss of mild steel specimen with inhibitor, A is area of MS specimen and t is immersion time. Table 1 shows that corrosion rates of mild steel decrease with increase in concentration of AEZJR inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature.[19]

3.2 Inhibition efficiency

From the obtained corrosion rates, inhibition efficiencies were calculated by using following equation (2).[1, 34]

\[
IE\% = \left(\frac{CR_{Blank} - CR_{inh}}{CR_{Blank}}\right) \times 100
\]

(2)

Where CR_{Blank} is the corrosion rate in absence of inhibitor and CR_{inh} is corrosion rate in presence of inhibitor. AEZJR are given in Table 1. Data in Table 1 show that %IE increase with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion.[20] Further the decrease in % I.E. with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place.[35] 62.68% inhibition efficiency is observed at 8% (v/v) concentration of inhibitor.

Table 1 Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of AEZJR at different temperatures

<table>
<thead>
<tr>
<th>C_{inh} (v/v)%</th>
<th>CR x 10^{-3} (g cm^{-2} min^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303 K</td>
</tr>
<tr>
<td>0</td>
<td>0.67</td>
</tr>
<tr>
<td>1</td>
<td>0.56</td>
</tr>
</tbody>
</table>
Table 2 Inhibition efficiencies of AEZJR at different concentrations and temperatures in 1 M HCl solution

<table>
<thead>
<tr>
<th>C_{inh} (v/v%)</th>
<th>I E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303 K</td>
</tr>
<tr>
<td>1</td>
<td>16.42</td>
</tr>
<tr>
<td>2</td>
<td>44.78</td>
</tr>
<tr>
<td>3</td>
<td>47.76</td>
</tr>
<tr>
<td>5</td>
<td>56.72</td>
</tr>
<tr>
<td>8</td>
<td>62.69</td>
</tr>
</tbody>
</table>

The graph shows the variation of Inhibition Efficiency (IE) with different concentrations of C_{inh}.
3.3 KINETIC PARAMETERS

Assuming that corrosion rates of steel specimens against concentration of inhibitor obeys kinetic relationship as equation (3) [19,38]

\[ \log CR = \log K + B \log C_{inh} \]  

Where K is rate constant and equal to CR when inhibitor concentration is unity. B is reaction constant which is measure of inhibitor effectiveness and \( C_{inh} \) is the concentration v/v %(ml/100ml) of AEZJR. Figure 2 represents plot between log CR and log \( C_{inh} \) values at various studied temperatures. B and K were calculated by slope and intercept of straight lines obtained in Figure 1. The obtained results are summarized in Table 3 which can be discussed as follows [19] Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species. The high negative values of B reflects good inhibitive property of inhibitor High negative value of B can be observed as steep slope in graph (Fig.2).Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures. The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

**Table 3. Kinetic parameters for mild steel corrosion in 1 M HCl solution with AEZJR**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Kinetic Parameters</th>
<th>Kinetic Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>( K \times 10^{-3} ) (g cm(^2) min(^{-1}))</td>
</tr>
<tr>
<td>303 K</td>
<td>-0.372</td>
<td>0.52723</td>
</tr>
<tr>
<td>313 K</td>
<td>-0.278</td>
<td>1.279381</td>
</tr>
<tr>
<td>323 K</td>
<td>-0.124</td>
<td>2.118361</td>
</tr>
</tbody>
</table>

Figure 1. Variation in IE % for mild steel corrosion in 1M HCl at different concentration of AEZJR at different studied temperatures

Figure 2. Variation in log CR with log \( C_{inh} \) for mild steel corrosion in 1M HCl in presence of different concentration of AEZJR at various studied temperatures
Figure 3. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJR.

Figure 4. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJR.
3.4 THERMODYNAMIC AND ACTIVATION PARAMETERS

Thermodynamic and activation parameters like apparent activation energy $E_{act}$, enthalpy of activation $\Delta H^*$, entropy of activation $\Delta S^*$ were calculated for steel dissolution process. Activation energy $E_{act}$ were calculated by following Arrhenius equation (4)[34,35]

$$\log CR = \log A - \frac{E_{act}}{2.303RT}$$  \hspace{1cm} (4)\\

Where A is Arrhenius pre-exponential factor, $E_{act}$ is activation energy, R is universal gas constant, T is absolute temperature. The slope of log CR vs 1/T in Figure 3 gives the values of activation energies at studied concentrations. Table 4 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in $E_{act}$ for corrosion process in inhibitor solution further interpreted as physical adsorption of inhibitor species on mild steel surface.[16, 23, 25] Besides this According to Damaskin[47], the value of activation energy lesser than 80kJ/mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present study. The values of enthalpy of activation $\Delta H^*$ and entropy of activation $\Delta S^*$ were calculated by following transition state equation (5).[34,35]

$$\log_\text{e}(CR/T) = \log(R/Nh) + \frac{[\Delta S^*/2.303RT] - [\Delta H^*/2.303RT]}$$

Where h is planck’s constant, N is Avogadro number R is the gas constant A plot of log(CR/T) vs 1/T gave a straight line with slope of (-$\Delta H^*/2.303R$) and intercept of $[(log R/Nh) + (\Delta S^*/2.303 R)]$ from which the values of $\Delta H^*$ and $\Delta S^*$ were calculated (see Figure 4). These values are tabulated in Table 4. Values of $\Delta H^*$ were found positive. Positive values indicate endothermic nature of steel dissolution process.[1, 17, 35] Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with increase in temperatures. Negative values of $\Delta S^*$ are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex.[1, 11, 30] It is also observed from data in Table 4 that $E_{act}$ and $\Delta H^*$ vary in the same manner. Values of both $E_{act}$ and $\Delta H^*$ increase with increase in concentration of inhibitor, suggesting that energy barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of $E_{act}$ as the concentration of inhibitor becomes greater.[1, 29, 31] The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume.[19]

Table 4. Activation and thermodynamic parameters for mild steel corrosion in 1 M HCL solution with AEZJR

<table>
<thead>
<tr>
<th>C_{inhin} (v/v)%</th>
<th>$E_{act}$ (kJ/mol)</th>
<th>$\Delta H^*$ (kJ/mol)</th>
<th>$\Delta S^*$ (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>42.72</td>
<td>39.88</td>
<td>-177.64</td>
</tr>
<tr>
<td>1.0</td>
<td>45.46</td>
<td>42.80</td>
<td>-170.56</td>
</tr>
<tr>
<td>2.0</td>
<td>55.28</td>
<td>52.72</td>
<td>-143.63</td>
</tr>
<tr>
<td>3.0</td>
<td>57.35</td>
<td>54.80</td>
<td>-137.55</td>
</tr>
<tr>
<td>5.0</td>
<td>61.98</td>
<td>59.47</td>
<td>-130.48</td>
</tr>
<tr>
<td>8.0</td>
<td>65.50</td>
<td>63.03</td>
<td>-118.53</td>
</tr>
</tbody>
</table>
3.5. ADSORPTION ISOTHERM AND GIBBS ENERGY

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage $\theta$ were fitted in different adsorption isotherms. Langmuir adsorption isotherm was the best fit. The mathematical expressions for Langmuir adsorption isotherm can be expressed by the following equation.[10,40,42-44]

$$\frac{\theta}{1 - \theta} = \frac{1}{K_{ads}} + C_{inh} \tag{6}$$

Rearranging the above equation (6) we get

$$\frac{\theta}{1 - \theta} = K_{ads}C_{inh} \tag{7}$$

$$\log \left( \frac{\theta}{1 - \theta} \right) = \log K_{ads} + \log C_{inh} \tag{8}$$

Where $K_{ads}$ is the equilibrium constant of adsorption, $\theta$ is the surface coverage, $(1 - \theta)$ is the uncovered surface, $C_{inh}$ is the concentration of inhibitor. Values of $K_{ads}$ were calculated from the intercept of Langmuir adsorption isotherm drawn according to the equation (8) between $\log \left( \frac{\theta}{1 - \theta} \right)$ and $\log C_{inh}$ (see Figure 5). The value of $K_{ads}$ obtained from Langmuir adsorption isotherm is related to Gibbs energy according to the following equation (9)[19, 38]

$$K_{ads} = \frac{1}{C_{H_2O}} \exp \left( \frac{-\Delta G_{ads}}{RT} \right)$$

It can be written as:

$$\Delta G_{ads} = -2.303 RT \log \left( K_{ads}. C_{H_2O} \right) \tag{10}$$

Where $C_{H_2O}$ is the concentration of water in (ml / L) at metal/solution interface, $R$ is universal gas constant and $T$ is absolute temperature. The values of $\Delta G_{ads}$ were tabulated in Table 5. Obtained values of Gibbs energy were plotted against temperature in accordance with the following basic equation.[19,39]

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \tag{11}$$
Intercept of graph between $\Delta G_{ads}$ vs $T$ in Figure 7 gives value of $\Delta H_{ads}$ and by putting the value of intercept in equation (11) values of $\Delta S_{ads}$ were obtained. These obtained adsorption parameters Gibbs free energy of adsorption ($\Delta G_{ads}$), enthalpy of adsorption ($\Delta H_{ads}$) and entropy of adsorption ($\Delta S_{ads}$) are listed in Table 5. $\Delta G_{ads}$ values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface.[1,4,5,7,19,28] Generally values of $\Delta G_{ads}$ upto -20 KJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 KJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption).[1,4, 5, 12, 13, 21, 22, 33] The obtained values of $\Delta G_{ads}$ were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface.[1, 25, 33] Values of $\Delta H_{ads}$ has been found negative indicating the exothermic adsorption process[11,14,16,20,34] which further indicates lower %IE at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or chemical adsorption or mixture of both.[3] In exothermic process, values of $\Delta H_{ads}$ predict physi sorption or chemisorption. For physi sorption values of $\Delta H_{ads}$ is lower than 40kJ/mol while for chemisorption it approaches to 100kJ/mol.[36,2] Values of $\Delta H_{ads}$ in Table 5 indicate physi sorption. Negative values of $\Delta S_{ads}$ indicate decrease in entropy of adsorption process. This behavior can be explained as follows: Before the adsorption of inhibitor molecules onto mild steel surface, they might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed.[13] A more interesting behavior is observed in Table 5 that negative $\Delta H_{ads}$ value is accompanied with negative $\Delta S_{ads}$ value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vice versa.[20,35] The obtained positive values of $\Delta S_{ads}$ are the algebraic sum of the adsorption of organic molecules and the desorption of water molecules.[15, 46] Therefore the positive values of entropy of adsorption is the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy.[45]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta G_{ads}$ (kJ/mol)</th>
<th>$\Delta H_{ads}$ (kJ/mol)</th>
<th>$\Delta S_{ads}$ (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 K</td>
<td>-7.84794</td>
<td></td>
<td>-89.8748</td>
</tr>
<tr>
<td>313 K</td>
<td>-7.05217</td>
<td>-35.08</td>
<td>-89.5458</td>
</tr>
<tr>
<td>323 K</td>
<td>-5.7499</td>
<td></td>
<td>-90.8053</td>
</tr>
<tr>
<td>333 K</td>
<td>-5.28394</td>
<td></td>
<td>-89.4777</td>
</tr>
</tbody>
</table>

Table 5 Adsorption parameters for mild steel corrosion in 1 M HCl solution with AEZJR
Figure 6. Freundlich adsorption isotherms of AEZJR on mild steel surface in 1M HCl at different studied temperatures

\[
\Delta G_{\text{ads}} (\text{kJ/mol}) \quad T (\text{K})
\]

T = 303 K

Figure 7. The Variation of $\Delta G_{\text{ads}}$(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AEZJR

4. CONCLUSIONS
1. Result showed that AEZJR is good corrosion inhibitor for mild steel in 1M HCl solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiencies increases at lower temperature suggest the physiorption process of inhibitor on mild steel surface.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests physiorption.
5. Enthalpy of adsorption comes out to be negative and lower than 40kJ/mol, which shows exothermic and physical adsorption process of inhibitor.
6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1 M HCl in AEZJR.

5. ACKNOWLEDGEMENT
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