Corrosion Inhibition of Mild Steel in Acidic Medium using High Altitude Plant Extract

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Abstract

Corrosion inhibition of methanol extract of Artemisia vulgaris on the corrosion of mild steel in 1M H₂SO₄ has been investigated using weight loss measurements. The inhibition efficiency increases with increase in concentration and decreases with increase in temperature beyond 308 K. Adsorption of extract on metal follows Langmuir adsorption isotherm. The activation and free energies for the inhibition reactions support the mechanism of physical adsorption. Values of enthalpy and entropy supports that the process is endothermic and spontaneous. Surface and protective film analysis have been carried out by energy dispersive x-ray (EDX) and scanning electron microscopy (SEM).

Keywords: Artemisia, inhibitor, mild steel, thermodynamic

Introduction

Mild steel has wide spread application in a broad field of industry and machinery due to its availability and low cost. Acid solutions are extensively used in the processes such as acid pickling, cleaning of boilers, descaling and drilling operations in oil and gas industries. Base metal applied in these processes undergoes undesirable dissolution. In order to reduce metal dissolution, various means like surface modification, alloy formation are adopted. However, more accepted practice for the reduction of corrosion is the use of inhibitors which when added in small amount retards rate of corrosion significantly and prevents from economic loss due to metallic corrosion. A substance to be used as corrosion inhibitor must fulfil some requirements. An inorganic compounds must be able oxidize the metal, forming a passive layer on its surface. Organic molecules should have feature like a large structure, double bonds, an active centre or groups which gives them to be adsorbed on metal surface by displacing water molecules and cover a large area of a metal surface with a compact barrier film. In chemisorption, electron transfer from inhibitor to metal to form coordinate covalent bond is facilitated by the presence of lone pairs or π electrons in inhibitor molecules.

Many organic and synthetic chemical containing oxygen, sulphur, nitrogen are studied as corrosion inhibitor and found effective as well. Unfortunately, most of them are hazardous to human and

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environment during their synthesis or application. This motivates investigations to develop non toxic, biodegradable, environmentally acceptable, renewable and cheap inhibitor as the demand of recent awareness of green chemistry. These requirements may be achieved in the inhibitor prepared from different parts of plant extracts. Phytochemicals present in plant extracts have similar molecular and electronic structures to the conventional organic inhibitor molecules. Many investigations reveal that plant extracts can be used as effective green inhibitor such as henna, coconut, olive, Cassia auriculata, Aloe, Hunteria umbellata, Progostemon benghalensis etc. Plant extracts shows inhibitions efficiency due to presence in their composition of complex organic species such as alkaloids, flavonoids, polyphenol, tannins, nitrogen bases, carbohydrates, protein as well as hydrolysis products.

Like in chemical reactions, rate of corrosion increases with increase in temperature. Acid pickling is done usually at elevated temperature up to 60 °C in HCl and up to 90°C in H2SO4. Some conclusion regarding mechanism or inhibiting action can be drawn from the temperature dependence of the inhibitor efficiency and the comparison of the obtained thermodynamic data of the corrosion process in both presence and absence of inhibitor. So, the effect of temperature on a corrosion process has practical and theoretical importance.

**Experimental Methods**

**Preparation of specimens**

A flat sheet of mild steel available from mild steel supplier of Kathmandu valley was cut into coupons of diameter 4 cm×4 cm×0.15cm. The coupons were polished with silicon carbide paper of different grades, starting with coarse one (100 grade) and proceeding in steps to finest (1500 grade). Dimension of each coupons were measured with digital vernier calliper, ultrasonicated in ethanol, dried and stored in moisture free desiccators.

**Preparation of methanol extract**

Aerial parts of *Artemisia vulgaris* were collected from Gundu, Bhaktapur, shade dried and powdered. 200 g of powder was extracted with methanol for 72 hrs followed by filtration to obtain extract as filtrate. Process was repeated until colourless extract was obtained. The extract was initially concentrated using rotary evaporator then dried on water bath to obtain solid residue.

**Preparation of solution**

1 M H2SO4 was prepared by diluting 55.6 mL concentrated H2SO4 in 1 litre volumetric flask up to the mark with distilled water. 1 g extract was dissolved in 1000 mL 1 M H2SO4 at 318 K temperature. Undissolved extract was removed by filtration. Filtrate was taken as 1000 ppm stock solution of acid in presence of inhibitor. Stock solution was diluted with calculated volume of 1M H2SO4 to prepare solution of different concentration of 800, 600, 400 and 200 ppm.

**Weight loss measurements**

The different parameters used for the study by weight loss measurements were effect of time, concentration of inhibitor solution and temperature. Polished coupons were removed from desiccators and weights were taken in an electronic balance. Weighed coupons were immersed in 100 mL acid (1 M H2SO4) without and with 1000 ppm concentration of the inhibitor in different beakers for various time
intervals (3, 6, 9, 12 and 24 hours) at same temperature 298 K to study the effect of time in inhibition efficiency. To study effect of concentration, weighed coupons were immersed in 100 mL acid (1 M H_{2}SO_{4}) without and with different concentrations of inhibitor (1000, 800, 600, 400, 200 ppm) in different beakers for 6 hours at same temperature 298 K. Similarly, effect of temperature was studied by immersing polished coupons in 100 mL acid (1 M H_{2}SO_{4}) without and with 1000 ppm concentration of the inhibitor in different beakers for 6 hours at various temperatures (298K, 308K, 318K, 328K, 338K). Temperature in experiments was adjusted by using clifton water bath model no. NE2-4D. After the elapsed time, coupons were taken out, washed thoroughly with distilled water, rinsed with acetone, dried, stored in desiccators and reweighed. All experiments were in triplicates and illustrated data are mean values of obtained results.

The corrosion rate (CR), surface coverage (θ) and inhibition efficiency (IE%) were calculated using following equations:

\[
CR = \frac{87.6W}{AtD}
\]
\[
θ = \frac{W_1 - W_2}{W_1}
\]
\[
IE\% = \left(1 - \frac{W_2}{W_1}\right) \times 100
\]

**Surface analysis**

Three polished coupons were immersed in acid solution without and with inhibitor of 400 and 1000 ppm concentrations for 24 hours. Then coupons were washed, dried and stored in desiccators.

**SEM analysis**

Surface analysis of mild steel coupons were performed using scanning electron microscope at 500x magnification at three different locations to ensure reproducibility. It was performed by using Bio-Logic M470 Ac-SECM scanning electron microscope.

**Energy dispersive x-ray (EDX) analysis**

Energy dispersive x-ray (EDX) analysis was carried out with Bio-Logic M470 Ac-SECM scanning electron microscope in conjugation with an energy dispersive spectrometer employing beam of accelerating voltage 15 KV to examine surface film formed on the metal specimen.

**Results and Discussion**

**Effect of immersion time**

Corrosion rate and inhibition efficiency by methanol extract of *Artemisia vulgaris* in various times are calculated from weight loss data is shown in table 1 and represented in figure 1. Result shows that
corrosion rate is inhibited by extract which is due to adsorption of photochemical present in extract. Inhibition efficiency decreases gradually with increase in time of immersion. It is almost same at 3 and 6 hrs. On the basis of table 1, weight loss for 15 g mild steel coupon with 30 cm² surface area is calculated when coupon was immersed in acid with and without inhibitor and plot of weight loss of coupon in different time is shown in figure 2. This data clearly shows that loss of metal by using inhibitor is decreased. This data reveals that adsorbed compounds starts desorption from metal surface after certain time and more metal surface is exposed to acidic media.

Table 1 : Corrosion rate of mild steel and inhibition efficiency of *Artemisia vulgaris* for mild steel corrosion at various time

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Corrosion Rate (mg/cm²h)</th>
<th>Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For Acid without inhibitor</td>
<td>For acid with inhibitor</td>
</tr>
<tr>
<td>3</td>
<td>55.47</td>
<td>17.66</td>
</tr>
<tr>
<td>6</td>
<td>59.50</td>
<td>19.15</td>
</tr>
<tr>
<td>9</td>
<td>57.65</td>
<td>22.20</td>
</tr>
<tr>
<td>12</td>
<td>54.04</td>
<td>23.62</td>
</tr>
<tr>
<td>24</td>
<td>50.15</td>
<td>24.37</td>
</tr>
</tbody>
</table>

**Figure 1:** Variation of inhibition efficiency with different immersion times of *A. vulgaris* extract on mild steel surface

**Figure 2:** Variation in weight of mild steel immersed in acid with and without inhibitor
Effect of Concentration

Corrosion rate and inhibition efficiency by methanol extract of *Artemisia vulgaris* in various concentration at 298 K for 6 hours are calculated from weight loss data is shown in table 2 and represented in figure 3.

**Table 2:** Corrosion rate of mild steel and inhibition efficiency of *Artemisia vulgaris* for mild steel corrosion at various concentration

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Corrosion Rate</th>
<th>Inhibition efficiency</th>
<th>Surface Coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank (0)</td>
<td>59.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>39.52</td>
<td>33.58</td>
<td>0.336</td>
</tr>
<tr>
<td>400</td>
<td>31.30</td>
<td>47.39</td>
<td>0.474</td>
</tr>
<tr>
<td>600</td>
<td>26.77</td>
<td>55.00</td>
<td>0.550</td>
</tr>
<tr>
<td>800</td>
<td>21.78</td>
<td>63.40</td>
<td>0.634</td>
</tr>
<tr>
<td>1000</td>
<td>19.15</td>
<td>67.81</td>
<td>0.678</td>
</tr>
</tbody>
</table>

![Figure 3: Variation of inhibition efficiency with different concentration of *A. vulgaris* extract on mild steel surface](image)

Results show that inhibition efficiency increases with increase in concentration of inhibition in acid. It is due to the more surface coverage of mild steel with more adsorption of phytochemical compounds on it.

**Adsorption isotherm**

Adsorption isotherm provides the basic information on the interaction between the inhibitor and mild steel surface since inhibition efficiency is due to adsorption of compounds on metal surface through their polar functions making a barrier for charge and mass transfer between the metal and the environment.
Water molecules are adsorbed on metal surface in aqueous solution. So, the adsorption of inhibitor molecules from aqueous solution is a quasi substitution process. The linear relation between $\theta$ value and $C_{inh}$ (concentration of inhibitor) should be known to find the adsorption isotherm. To fit $\theta$ Value, attempts were made to various isotherms including Langmuir, Tempkin, Freundlich, El-Awady. Both value of linear correlation coefficient ($R^2$) and slope is almost equal to 1 in Langmuir adsorption isotherm shown in figure, which indicates that mono-layer of the inhibitor have been adsorbed on metal surface without interaction between the adsorbed molecules.

![Figure 4: Langmuir adsorption isotherm plot for mild steel in 1 M H$_2$SO$_4$ with different concentration of A. Vulgaris extract.](image)

According to Langmuir adsorption isotherm equation, 
\[
\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh},
\]
value of adsorption constant $K_{ads}$ is calculated from intercept of straight line. This value can be used in the equation, $\Delta G^0 = -RT \ln(55.5K_{inh})$ to calculate the value of free energy of adsorption ($\Delta G^0$), where 55.5 is concentration of water in solution in mol/L and R is universal gas constant (8.314J/mol K). Calculated value of $\Delta G^0$ according to relation is -12.22 KJ/mol. which is less than the threshold value -40 KJ/mol required for chemisorption. Value of $\Delta G^0$ less than or around -20 KJ/mol means adsorption is physical adsorption. So, adsorption of Artemisia vulgaris extract is physical adsorption.

**Effect of temperature**

Corrosion rate and inhibition efficiency by 1000 ppm methanol extract of Artemisia vulgaris in various temperature for 6 hours are calculated from weight loss data is shown in table 3 and represented in figure 5. IE increases with increase in temperature up to 308 K and beyond this IE decreases. Decrease in IE with increase in temperature might be due to desorption or decomposition inhibitor at higher temperature (14). This data also supports the adsorption is physical adsorption.
Figure 5: Variation of inhibition efficiency of A. vulgaris extract on mild steel surface at different temperature.

Table 3: Corrosion rate of mild steel and inhibition efficiency of Artemisia vulgaris for mild steel corrosion at various temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Corrosion Rate (mg/cm²h)</th>
<th>Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For Acid without inhibitor</td>
<td>For acid with inhibitor</td>
</tr>
<tr>
<td>298</td>
<td>92.40</td>
<td>26.06</td>
</tr>
<tr>
<td>308</td>
<td>136.86</td>
<td>35.91</td>
</tr>
<tr>
<td>318</td>
<td>206.98</td>
<td>95.20</td>
</tr>
<tr>
<td>328</td>
<td>264.48</td>
<td>147.47</td>
</tr>
<tr>
<td>338</td>
<td>332.83</td>
<td>203.85</td>
</tr>
</tbody>
</table>

Calculation of activation energy and thermodynamic parameters

The activation energy (Eₐ) can be calculated from Arrhenius plots for corrosion rate at different temperature according to relation : 

[\log(C.R.) = \log A - \frac{E_a}{2.303 RT}]

Where, A is the Arrhenius pre-exponential constant, T is absolute temperature.

From the Arrhenius plot shown in figure , Calculated values of Eₐ for acid without and with inhibitor are 27.09 KJ/mol and 46.38 KJ/mol respectively and value of A for acid without and with inhibitor are 5382697.8 mg/Cm² and 3296097122 mg/Cm² respectively. Increase in Eₐ with addition of inhibitor shows the strong adsorption of inhibitor molecules on the metal surface (15). This value is lower than threshold value of 80KJ/mol, required for chemisorption. This indicates that adsorption is physical adsorption.

An alternative form of Arrhenius equation is transition state equation :
\[
\log \left( \frac{C.R.}{T} \right) = \left[ \log \left( \frac{R}{hN} \right) + \left( \frac{\Delta S^*}{2.303R} \right) - \frac{\Delta H^*}{2.303RT} \right]
\]

Where h is plank's constant, 6.6261×10⁻³⁴ Js and N is the Avogadro's number, 6.0225×10²³ mol⁻¹

The slope of straight line obtained by plotting \(\log(C.R./T)\) vs. \(1/2.303T\) shown in figure is enthalpy of activation (Δ\(H^*\)) and the entropy of activation (Δ\(S^*\)) can be calculated from its intercept. Calculated values of \(\Delta H^*\) for acid without and with inhibitor are 24.45 KJ/mol and 43.75 KJ/mol respectively. Positive value of \(\Delta H^*\) indicates the endothermic nature of metal dissolution process. Increase in value of \(\Delta H^*\) with addition of inhibitor shows the decrease in corrosion rate is controlled by kinetic parameters of activation. (16). Above calculations show that value of \(E_a\) is higher than that of \(\Delta H^*\), which indicates the involvement of a gaseous reaction, simply the hydrogen evolution reactions, resulting the decrease in the total reaction volume\(^{17}\). The corrosion process is unimolecular in the condition, \(E_a - \Delta H^* = RT\). Here difference in value of \(E_a - \Delta H^*\) is 2.64 KJ/mol which is nearly equal to RT.

Calculated value of \(\Delta S^*\) for acid without and with inhibitor are -124.91 J/mol K and -71.50 J/mol K respectively. Large and negative values of \(\Delta S^*\) indicates that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex. In acid, transition state of the rate determining recombination step represents a more orderly arrangement relative to the initial state so a high value for the \(\Delta S^*\) is obtained. In presence of inhibitor, the surface is covered with adsorbed molecules and rate of discharge of hydrogen ions in rate determining step is decreased resulting the system to pass from random arrangement, hence value of \(\Delta S^*\) is increased. The increase in value of \(\Delta S^*\) with addition of inhibitor implies the increase in disorder on going from reactant to activated complex. This behaviour is due to replacement of water molecules during adsorption of extract on metal surface\(^3\).

\(\text{Figure 6} : \text{Arrhenius plot for mild steel in } 1\ M\ \text{H}_2\text{SO}_4 \text{ with and without } A.\ \text{vulgaris extract}\)

\(\text{Figure 7} : \text{Transition state plot for mild steel in } 1\ M\ \text{H}_2\text{SO}_4 \text{ with and without } A.\ \text{vulgaris extract}\)
Surface analysis

Energy dispersive x-ray (EDX) is employed to get the information about the composition of the surface of mild steel sample immersed in acid without and with inhibitor for 24 hours. The results are shown in figure 8. Percentage composition of different elements present in metal surface is listed in table 4. Data shows that there is decrease in iron and increase in N, C and O on surface of mild steel in sample immersed in acid with inhibitor which indicates the formation of protective film due to adsorption of phytochemicals containing N, C and O on surface and inhibit the iron dissolution.

Figure 8: EDX spectra of mild steel coupons after 24 hr. immersion in (a) 1 M H₂SO₄ (b) 400 ppm extract solution in 1 M H₂SO₄ (c) 1000 ppm extract solution in 1 M H₂SO₄

Table 4: Percentage of weight of different element on the mild steel surface after immersing in sample in different solution.

<table>
<thead>
<tr>
<th>Surface dipped in</th>
<th>Iron</th>
<th>Carbon</th>
<th>Nitrogen</th>
<th>Oxygen</th>
<th>Phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished metal sample</td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid without inhibitor</td>
<td>97.45%</td>
<td>1.72%</td>
<td></td>
<td>0.83%</td>
<td></td>
</tr>
<tr>
<td>Acid with inhibitor of 400 ppm</td>
<td>94.8%</td>
<td>1.78%</td>
<td>1.31%</td>
<td>2.11%</td>
<td></td>
</tr>
<tr>
<td>Acid with inhibitor of 1000 ppm</td>
<td>92.91%</td>
<td>2.27%</td>
<td>1.58%</td>
<td>3.16%</td>
<td>0.07%</td>
</tr>
</tbody>
</table>

Figure 9: SEM micrographs of mild steel coupons after 24 hr. immersion in (a) 1 M H₂SO₄ (b) 400 ppm extract solution in 1 M H₂SO₄ (c) 1000 ppm extract solution in 1 M H₂SO₄
To study the surface morphology of mild steel, Scanning electron microscope (SEM) images of coupon immersed for 24 hours in acid without and with inhibitor were taken by Bio-Logic M470 AC-SECM scanning electron microscope. In SEM image of surface of metal sample immersed in acid without inhibitor shown in figure 9, surface was highly porous with deep and large cracks but surface was relatively smooth by the formation of protective film on surface when immersed for same time after addition of inhibitor.

Conclusions

1. Artemisia vulgaris extract acts as a good inhibitor for corrosion of mild steel in 1 M \text{H}_2\text{SO}_4 solution.
2. Inhibition efficiency increases with increase in concentration and decreases with increase in temperature beyond 308 K.
3. The adsorption of extract on mild steel follows the Langmuir adsorption isotherm.
4. Values of $\Delta G^\circ$ and $E_a$ indicates the adsorption of molecules on metal surface through physical adsorption.
5. Values of $\Delta H^\circ$ and $E_a$ indicates that the corrosion process is unimolecular and rate is controlled by kinetic parameters of activation.
6. Values of $\Delta H^\circ$, $\Delta S^\circ$ indicates that adsorption process is spontaneous and endothermic.
7. EDX and SEM confirm the formation of protective film extract on metal surface and inhibit corrosion.

References