Kinetics and Thermodynamic Studies of Corrosion Inhibition of Mild Steel Using Methanolic Extract of *Erigeron floribundus* (Kunth) in 2 M HCl Solution

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**ABSTRACT**

The investigation of kinetics and thermodynamics of the corrosion of a mild steel in a 2 M HCl solution using methanolic extract of *Erigeron floribundus* was carried out by means of gravimetric techniques. The results obtained indicate that the extract retarded corrosion. The inhibition efficiency was seen to increase with increase in concentration of the inhibitor, as well as with increase in temperature. The values of activation energy \((E_a)\) obtained indicate a chemisorption mechanism, whereas the value of Gibbs free energy \((\Delta G_{ads}^{o})\) indicates a spontaneous adsorption of the extract components on the metal surface. Kinetic modelling of the experimental data obeys first order reaction. The adsorption of methanolic extract of *Erigeron floribundus* onto the mild steel surface followed the Langmuir adsorption isotherm model. Therefore, the extract functions as a good corrosion inhibitor for mild steel in hydrochloric acid.

**Keywords:** *Erigeron floribundus*, corrosion inhibition, kinetics, Adsorption mechanism
1. INTRODUCTION

![Image](https://inpn.mnhn.fr/espece/cd_nom/611690)

Figure 1. *Erigeron floribundus* (Kunth)
https://inpn.mnhn.fr/espece/cd_nom/611690

Organic compounds containing polar functional groups such as nitrogen, sulfur and oxygen in conjugated system have been reported to be effective corrosion inhibitors for steel [1]. Some plants extracts contain a mixture of polar functional group and thus possess multiple active centers. The study of corrosion inhibition of plants’ extracts has been on the increase in recent times. Generally the inhibitive effect of plants extract is attributed to the adsorption of organic substances on the metal surface by blocking active sites or forming a protective barrier on steel surfaces [2, 3].

The effectiveness of inhibition by the adsorbed inhibitor system will be determined by the energy released on forming the metal-inhibitor bond compared to the corresponding changes when the pure acid reacts with the metal [1, 4]. In recent years, natural compounds, such as
herbal plants are employed as corrosion inhibitor, in order to develop new cleaning chemicals for green environment, *Erigeron floribundus* is well known and reputed medicinal plant traditionally used for the treatment of skin disorders by the rural population as well as those from the urban area. This species is widespread in Nigeria [5, 6]. The main purpose of this study is to investigate the inhibitive potential of methanolic extract of *Erigeron floribundus* as an eco-friendly corrosion inhibitor on a mild steel in 2 M HCl solution using gravimetric technique. The summary of plants extracts used as corrosion inhibitors have recently been given in [1-5] and [7-16] (Figure 1).

2. EXPERIMENTAL METHODS

2.1 Preparation of specimen

Mild steel specimens, had a composition of 0.6% Mn; 0.36% P; 0.15% C; 0.07% S, and 98.79% Fe, and the specimens used in this work were obtained from Physics Department, University of Calabar - Nigeria. The mild steel was mechanically pressed and cut to coupons of dimension 40.0 × 12.0 × 0.8 mm, with the surface area of 10.10 cm².

2.2 Preparation of the plant extract

The fresh parts of *Erigeron floribundus* were obtained within the premises of Faculty of Agriculture Cross River University of Technology, Calabar. The fresh plant was washed with water, air dried, powdered and extracted with methanol for 24 hours. The methanol solution was filtered and refluxed further to obtain a concentrated solution. The clear dark brown methanol concentrated solution was dried under vacuum to get a semi-solid liquid [14]. 8 g of semi-solid liquid, that is methanol extract, was dissolved in 2 M HCl solution and kept for 24 hours. The resultant solution was filtered and stored. From the stock solution (8 g /L), inhibitor test solutions of concentrations: 0.1, 0.5, 1.0, 2.0, and 4.0 g /L were prepared using serial dilution method. These solutions were then used for the corrosion test [15].

2.3 Gravimetric measurement

Weighed test specimens were fully immersed separately for 5 hours in each of the beakers containing the extract for the five sets, the same process as above was done for the beaker containing only 2 M HCl solution. Each of the test specimens was taken out every one hour, washed with distilled water, raised with ethanol, dried in acetone, and re-weighed [7]. From the weight loss data, the corrosion rates (CR) were calculated from eq. 1:

\[
CR = \frac{WL}{A \cdot t} \times 1000 \text{ (mg·cm}^{-2} \cdot \text{h}^{-1})
\]

where \(WL\) is the weight loss data, \(A\) the specimen surface area, and \(t\) the immersion period.

Thus from corrosion rate, the inhibition efficiency \(IE\%\) was evaluated using eq. 2.

\[
IE\% = \frac{CR(\text{blank}) - CR(\text{inh})}{CR(\text{blank})} \times 100
\]
where $IE\%$ is the inhibition efficiency, $CR_{\text{blank}}$ is the corrosion rate for the blank, while $CR_{\text{inh}}$ is the corrosion rate for inhibited solution [8].

3. RESULTS AND DISCUSSION

3.1. Effect of temperature on corrosion inhibition of mild steel in 2 M HCl solution

The variation of weight loss $WL$, corrosion rate $CR$ and inhibition efficiency $IE\%$ obtained from experimental measurements of mild steel after immersion in 2 M HCl solution at the temperature of 303 K, 313 K, 323 K, and 333 K, as a function of concentration in the presence of methanol extract of *Erigeron floribundus*, is shown in Figs. 1, 2, and 3.

The results show that weight loss and corrosion rate values decrease from uninhibited to inhibited solution at each temperature. The decrease is payable to the inhibitive effect of the plant extract and these effects increased with an increase in concentration of the plant extract. Inspection of Fig. 3 reveals that the inhibition efficiency increases with increase in the concentration of the methanol extract, and increases with increase in temperature.

This could be attributed to the phytochemical components present in the plant extract, which were adsorbed in the mild steel-solution interface [6]. Inhibition efficiency and corrosion rate of the mild steel in various concentrations of methanol extract with temperature are summarized in Table 1.

![Fig. 1. Variation of weight loss of Mild steel in 2 M HCl solution as a function of concentration in the presence of methanol of *Erigeron floribundus* extract](image-url)
Fig. 2. Variation of corrosion rate of Mild steel in 2 M HCl solution as a function of concentration in the presence of methanol of Erigeron floribundus extract.

Fig. 3. Variation of inhibition efficiency of Mild steel in 2 M HCl solution as a function of concentration in the presence of methanol of Erigeron floribundus extract.
Table 1. Effect of various temperatures on a mild steel corrosion in 2 M HCl solution containing various concentrations of methanol extract of *Erigeron floribundus*.

<table>
<thead>
<tr>
<th>Con (g/L)</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IE%</td>
<td>CR(mg/h)</td>
<td>IE%</td>
<td>CR(mg/h)</td>
</tr>
<tr>
<td>BLANK</td>
<td>0.099</td>
<td>0.099</td>
<td>0.148</td>
<td>0.165</td>
</tr>
<tr>
<td>0.1</td>
<td>24.2</td>
<td>0.075</td>
<td>16.6</td>
<td>0.082</td>
</tr>
<tr>
<td>0.5</td>
<td>37.3</td>
<td>0.062</td>
<td>33.3</td>
<td>0.066</td>
</tr>
<tr>
<td>1.0</td>
<td>68.6</td>
<td>0.031</td>
<td>66.6</td>
<td>0.033</td>
</tr>
<tr>
<td>2.0</td>
<td>83.8</td>
<td>0.016</td>
<td>75.7</td>
<td>0.024</td>
</tr>
<tr>
<td>4.0</td>
<td>86.8</td>
<td>0.013</td>
<td>83.8</td>
<td>0.016</td>
</tr>
</tbody>
</table>

3.2. Kinetics and thermodynamics of the corrosion inhibition of mild steel in 2 M HCl solution

The corrosion rate of most reactions increases as temperature is increased, like the corrosion rate displayed in Table 1. It has been found experimentally that a plot of ln k against 1/T gives a straight line. This behaviour is normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the expression as eq. 3

\[ \ln k = \ln A - \frac{E_a}{RT} \]

where \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, collectively this two quantities are called Arrhenius parameters, while \( R \) is gas constant, \( T \) is absolute temperature, \( k \) represents the rate constant or corrosion rate [17].

The Arrhenius plot obtained from eq.3 gave a straight line graph, as shown in Fig. 4, with the slope of \(-E_a / 2.303 R\). Analysis of temperature dependence of inhibition efficiency, as well as comparison of the corrosion activation energies in the absence and presence of inhibitor gives insight into the possible mechanism of inhibitor adsorption. An increase in inhibition efficiency with a rise in temperature, with analogous decrease in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of formation of chemically adsorption film, whereas a decrease in inhibition efficiency with rise in temperature, with corresponding increase in corrosion activation energy in the presence of inhibitor compared to its absence, is recognized as a physical adsorption mechanism [6,11]. The inhibition efficiency with temperature, obtained in Table 1 and Fig. 3, suggests chemisorption of the phytochemical constituents of the plant extract on the surface of the metal. In order to confirm this, corrosion activation energies, \( E_a \) for the mild steel dissolution in 2 M HCl solution, in the absence and presence of the methanol extract, were obtained from the plot.
of \( \ln CR \) versus \( 1/T \) and are listed in Table 2. In the corrosion of mild steel in 2 M HCl solution weight at time after post treatment of coupons is chosen as \( w_f \), when \( \frac{w_f}{w_o} \) was plotted against time, in hours, a linear variation was observed, which confirms the first order reaction kinetics with respect to the mild steel in 2 M HCl solution, formulated as

\[
\ln \frac{w_f}{w_o} = -k \cdot t
\]

where \( w_o \) is the initial weight before immersion, \( k \) is the rate constant, and \( t \) is time. The values of the rate constants, obtained from the slopes of the plot in Fig. 5, are obtainable in Table 2.

Table 2. Calculated values of activation energy, enthalpy, entropy, rate constant, and half life for mild steel coupon in 2 M HCl solution containing methanol extract of Erigeron floribundus.

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>( E_a ) kJ/mol</th>
<th>( \Delta H ) kJ/mol</th>
<th>( \Delta S ) kJ/mol</th>
<th>Rate Con.</th>
<th>Half Life</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLANK</td>
<td>16.16</td>
<td>13.51</td>
<td>-22.67</td>
<td>4.12</td>
<td>0.422</td>
<td>0.999</td>
</tr>
<tr>
<td>0.1</td>
<td>8.59</td>
<td>59.54</td>
<td>-49.3</td>
<td>3.04</td>
<td>0.495</td>
<td>0.999</td>
</tr>
<tr>
<td>0.5</td>
<td>10.33</td>
<td>-36.76</td>
<td>-82.84</td>
<td>2.20</td>
<td>0.552</td>
<td>0.988</td>
</tr>
</tbody>
</table>
The results obtained reveal that the rate constant decreases with the increase in concentration of methanol extract of *Erigeron floribundus*. From the rate constant values, the half life values, $t_{1/2}$ of the metal in the test solutions were calculated from the equation 5:

$$t_{1/2} = \frac{0.693}{k}$$

and the deduced data are also listed in Table 2. The half life values were observed to increase with the increase in concentration of the methanol extract of *Erigeron floribundus*, indicating decrease in the dissolution rate of the metal in the solution with the increase in concentration of the inhibitor.

The transition state equation was used to calculate some thermodynamic parameters ($\Delta H_{ads}$ and $\Delta S_{ads}$) for the adsorption of methanol extract of *Erigeron floribundus* on the mild steel surface.

$$CR = \frac{RT}{Nh} \exp \left( \frac{\Delta S}{R} \right) \exp \left( - \frac{\Delta H}{RT} \right)$$
where \( CR \) is the corrosion rate for mild steel in 2 M HCl solution, \( R \) is gas constant, \( T \) is the temperature, \( N \) is the Avogadro’s number, \( h \) is the Planck constant, \( \Delta S_{ads} \) is the entropy of the adsorption and \( \Delta H_{ads} \) is the enthalpy of adsorption of the inhibitor on the mild steel surface. From the logarithm of both sides of eq. 6, eq. 7 was obtained,

\[
\log \left( \frac{CR}{T} \right) = \log \frac{R}{N} - \frac{\Delta S_{ads}}{2.303R} - \frac{\Delta H_{ads}}{2.303R \cdot T}
\]

The plots of \( \log \left( \frac{CR}{T} \right) \) against \( \frac{1}{T} \) for methanol extract of *Erigeron floribundus* were linear, the slopes and intercept of the transition state plot (*Fig. 6*) are equal to \(-\Delta H_{ads} / 2.303R\) and \(\log \frac{R}{N} - \frac{\Delta S_{ads}}{2.303R}\), respectively. The values of \( \Delta H_{ads} \), calculated from the slope of the plot were positive in blank and 0.1 g/L, and negative in 0.5, 1.0, 2.0 g/L, and 4.0 g/L, \( \Delta H_{ads} \) values of adsorption of methanol extract of *Erigeron floribundus* on mild steel surface exhibited both, endothermic and exothermic reactions, respectively. On the other hand, the values of \( \Delta S_{ads} \), calculated from the intercept of the transition state plot, are negative. This shows that there is an increase in the degree of disorderliness, indicating that there is a bigger association of the inhibitor’s molecules rather than dissociation [2, 3].

![Graph](image)

*Fig. 6.* Variation of \( \log \left( \frac{CR}{T} \right) \) with \( \frac{1}{T} \) for the inhibition of mild steel corrosion in 2 M HCl solution by methanol extract of *Erigeron floribundus*

We observed a progressive raise in the thermodynamic parameters (\( \Delta H_{ads} \) and \( \Delta S_{ads} \)), presented in Table 2, with increasing in the concentration of methanol extract of *Erigeron floribundus* which confirms that methanol extract of *Erigeron floribundus* is the adsorption inhibitor for the corrosion of mild steel in 2 M HCl solution.
3.3. Adsorption behaviour

The experimental inhibition of the corrosion of mild steel in 2 M HCl solution increases with increase in the concentration of the extract, and this can be explained by the adsorption of the constituent of the extract on the metal surface. From a hypothetical point of view, the inhibition action of the organic molecules has been regarded as a simple substitution process, in which an inhibitor molecule in aqueous phase substitution with any number of water molecules is adsorbed on the metal surface [7]

\[
\ln h + yH_2O \leftrightarrow \ln h_{(ads)} + yH_2O_{(aq)}
\]

The inhibitor molecules may then mingle with Fe\(^{2+}\) ions on the metal surface, forming metal-inhibitor complex. The resulting complex, depending on the relative solubility, could either inhibit or catalyse further metal dissolution. Methanol extract of the plant is viewed as an incredible rich source of naturally synthesized chemical compounds. These large numbers of different chemical components may form adsorbed intermediates (organic-metallic complexes) [7]. Most researchers claim that particular compound in a plant extract is solely responsible for the inhibition ability. In a real sense it is not true, since most plant extracts are composed of numerous organic compounds capable of either inhibiting or accelerating the corrosion processes. The net antagonistic and synergistic action of the phytochemical components of the plant is what is actually recorded as the inhibition efficiency of the methanol extract of the plant [4, 7].

Like most medicinal plants, Erigeron floribundus is composed of numerous naturally occurring compounds, with some of these compounds being isolated and characterized from the plant. These include: alkaloid, phenol, triterpenes, sterol, flavonoids, cardiac glycosides, and tannins [5, 6].

Most of these compounds have complex molecular structures, large molecular weight and significant number of oxygen, sulfur, and nitrogen atoms integrated in the structure. These compounds can adsorb on the metal surface through the lone pairs of the electrons present on their oxygen, sulfur, and nitrogen atoms. The adsorption of such compounds on the metal surface creates a barrier for charge and mass transfer, leading to a decrease in the interaction between the metal and the corrosive atmosphere. As a result, the corrosion rate of the metal decreases [12, 13].

The experimental data were applied to different adsorption isotherm models. It was found that the experimental data fitted the Langmuir adsorption isotherm (Fig. 7) which may be formulated as [9, 10]:

\[
\frac{C_{inh}}{\theta} = \frac{1}{b_{ads}} + C_{inh}
\]

where \(\theta\) is the surface coverage, \(C_{inh}\) is the concentration of the inhibitor and \(b_{ads}\) is the adsorption-desorption equilibrium constant. The adsorption-desorption equilibrium constant, obtained from the intercept of the Langmuir adsorption isotherm plots and linear regression coefficient were used to determine the best fit. The results obtained for \(\Delta G_{ads}\) and \(b_{ads}\) are shown in Table 3.
Table 3. Calculated values of equilibrium constant and free energy of the adsorption at different temperatures.

<table>
<thead>
<tr>
<th>Temp., K</th>
<th>$b_{ads}$</th>
<th>$\Delta G_{ads}$ kJ/mol</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>0.038</td>
<td>-39.72</td>
<td>0.998</td>
</tr>
<tr>
<td>333</td>
<td>0.036</td>
<td>-40.03</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Fig. 7. Langmuir adsorption isotherm of methanol extract of *Erigeron floribundus*.

The values obtained for $\Delta G^o_{ads}$ were negative indicating that the adsorption process is spontaneous. Generally, the values of $\Delta G^o_{ads}$ less than $-20 \text{ kJ} \cdot \text{mol}^{-1}$ signify physic-sorption and values more negative than $-40 \text{ kJ} \cdot \text{mol}^{-1}$ signifying chemisorptions [7, 9, 10]. The results listed in Table 3 show that $\Delta G^o_{ads}$ values are more negative than $-20 \text{ kJ} \cdot \text{mol}^{-1}$. This reveals that the adsorption of the inhibitor on the metal surface is spontaneous and confirms chemisorption’s mechanism.

4. CONCLUSIONS

The results presented in this paper show that the methanol extract from *Erigeron floribundus* inhibits the corrosion of mild steel in 2 M HCl solution to a reasonable extent. The
inhibition efficiency of the methanol extract increased with increasing concentration of the inhibitor with temperature. The inhibition process followed the first order reaction kinetics. It has been observed that the positive and negative values obtained for the enthalpy show a mixed reaction process such as endothermic and exothermic reactions. Also the value of entropy is negative, indicating association mechanism, and negative value of the free energy reveals that the reaction process is spontaneous. Adsorption isotherm mechanism followed the Langmuir adsorption.

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References


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