CORROSION INHIBITION BEHAVIOR OF KETOSULFONE FOR ZINC IN ACIDIC MEDIUM

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ABSTRACT
The corrosion inhibition behavior of Ketosulfone for zinc is investigated by polarization and AC-impedance techniques at 303-333K. The Tafel plots indicates that the Ketosulfone is a mixed type inhibitor. The interaction between metal and inhibitor is explained by Langmuir adsorption isotherm. \( \Delta G_{ads}^0 \) and \( \Delta H_{ads}^0 \) value indicates the electrostatic interactions between metal and inhibitor. Calculated activation parameters explains the corrosion process. SEM images show the difference between inhibited solutions and blank solution.

Key words: corrosion inhibitor; adsorption; Langmuir isotherm; Zinc.

1. INTRODUCTION
Zinc is a very important metal in the industry and domestic purposes and it is extensively used for galvanization process.

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Under aggressive conditions, zinc metal undergoes corrosion which gives the white colored rust [1-3]. The protection of metal from the corrosion is necessary in an acidic medium and alkaline medium. By using organic compounds, we can achieve protection of metals against corrosion. Compounds containing sulfur and nitrogen can be used for the corrosion inhibition of zinc in acid or nearly alkaline medium. The increase in the hydrogen overvoltage on the corroding metal is due to the presence of organic compounds [4-6]. Recently, the new type of corrosion inhibitors is developed to achieve the environmental regulations on industrial consumption and development thus, natural products, pharmaceutical ingredients and environment-friendly products, have gained much attention in regard to the development of green corrosion inhibitors that have high inhibition efficiency [7,8]. The drug ketosulfone is a very good corrosion inhibitor for the mild steel [9].

In the present work, the inhibiting action of ketosulfone for zinc in 0.1 M HCl has been done by various methods.

Ketosulfone is an anti-inflammatory drug. The presence of electron rich nitrogen, oxygen, sulfur atoms, and π-bonds in its structure are in favor of its adsorption on the metal surface, which gives scope to its study as a potential corrosion inhibitor.

The compound ketosulfone was purchased from Ramdev Chemicals India Pvt., Ltd., and Mumbai. IUPAC name of the ketosulfone is 1-(6-methylpyridine-3-yl) -2 (4-methylsulphonyl) phenyl ethanone. The structure of the molecule is as shown in Figure 1.

![Structure of ketosulfone](image.png)

**Fig 1.** Structure of 1-(6-methylpyridine-3-yl)-2(4-methylsulphonyl) phenyl ethanone (ketosulfone)

2. RESULTS AND DISCUSSION

Tafel Polarization measurements:
Fig.2. Tafel Plots for zinc in 0.1 M HCl in the absence and presence of different Inhibitor concentrations at (A) 303K(B) 313K(C) 323K(D) 313K temperatures.

The absolute corrosion rate can be measured by the electrochemical technique of polarization resistance and it is expressed in Milli-inches per year (mpy). Polarization resistance is also called as “linear polarization” [11].

The obtained Tafel plots are as shown in Figure 2. The electrochemical corrosion kinetic parameters such as corrosion potential \(E_{corr}\), corrosion current density \(i_{corr}\), cathodic Tafel slope \(\beta_c\), anodic Tafel slope \(\beta_a\) and inhibition efficiency \(\eta_p\) are reported in Table 1.

The corrosion current can be related directly to the corrosion rate through the following equation [12].

\[
\text{Corrosion Rate (mpy)} = \frac{0.13 \times i_{corr} \times F \times W}{d}
\]  

(1)
Where, \( E.W. \) = equivalent weight of the corroding species,
\( d \) = density of the corroding species.

The anodic or cathodic Tafel plots are described by the Tafel equation [13]:

\[
\eta = \frac{\beta \log t}{i_{corr}}
\]

\( \eta \) = overvoltage, the difference between the potential of the specimen and the corrosion potential.

\( \beta \) = Tafel constant.

The inhibition efficiency \( (\eta_p) \) was calculated from following relation

\[
\eta_p = \frac{i_{corr}^o - i_{corr}}{i_{corr}^o} \times 100
\]

Where, \( i_{corr}^o \) and \( i_{corr} \) are corrosion current in the absence and presence of inhibitor, respectively.

A potentiodynamic polarization plot, such can yield important information such as:

- The Tafel extrapolation method is very accurate which is equal or greater than conventional weight loss methods.
- It is possible to measure extremely low corrosion rates by using potentiodynamic polarization plots.
- A direct measure of the corrosion current can be provided by Tafel plots. As expected, As the increase in the concentration of inhibitor, The rate of corrosion was inhibited. The addition of the inhibitor which reduces the anodic reaction and also retards the cathodic reaction [14].

According to many literatures [15,16] the compound can be classified as an anodic or cathodic inhibitor, when the potential displacement is at least 85 mV with respect to the blank solution. In the present study the tafel plots indicate that the inhibitors are mixed type inhibitor.
Table 1. Tafel and AC impedance results for the corrosion of zinc in presence of different
Concentration of Ketosulfone in 0.1 M HCl.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Inhibitor con\textsuperscript{a} (ppm)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ mA cm\textsuperscript{-2}</th>
<th>Corrosion Rate (mpy)</th>
<th>$\beta_c$ mV/decade</th>
<th>$\beta_a$ mV/decade</th>
<th>$\eta_p$ (%)</th>
<th>$R_p$ cm\textsuperscript{2}</th>
<th>$C_{dl}$ (\mu F cm\textsuperscript{-2})</th>
<th>$\eta_z$ (%)</th>
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</thead>
<tbody>
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<td>16.3</td>
<td>1.903</td>
<td>7.315</td>
<td>8.399</td>
<td>-</td>
<td></td>
<td>72.57</td>
<td>0.047</td>
<td>-</td>
</tr>
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<td>14.7</td>
<td>1.715</td>
<td>7.773</td>
<td>9.019</td>
<td>9.8</td>
<td>85.12</td>
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</tr>
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<td>12.3</td>
<td>1.404</td>
<td>8.621</td>
<td>11.278</td>
<td>24.60</td>
<td>92.55</td>
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<td></td>
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<tr>
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<td>10.4</td>
<td>1.325</td>
<td>8.645</td>
<td>11.400</td>
<td>36.1</td>
<td>125.41</td>
<td>0.015</td>
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<td></td>
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<td>8.67</td>
<td>1.010</td>
<td>5.055</td>
<td>5.456</td>
<td>59.09</td>
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<td>1.65</td>
<td>6.028</td>
<td>6.442</td>
<td>35.7</td>
<td>87.59</td>
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<td>14.8</td>
<td>1.41</td>
<td>7.605</td>
<td>9.136</td>
<td>42.4</td>
<td>96.6</td>
<td>0.035</td>
<td>42.16</td>
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<td>1.12</td>
<td>7.868</td>
<td>9.650</td>
<td>45.9</td>
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<td>2.60</td>
<td>8.309</td>
<td>11.480</td>
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<td>61.11</td>
<td>0.072</td>
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<td>11.6</td>
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<td>9.543</td>
<td>18.8</td>
<td>75.34</td>
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<td>1.93</td>
<td>8.286</td>
<td>10.002</td>
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<td>7.235</td>
<td>3.873</td>
<td>31.8</td>
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<td>0.041</td>
<td>32.4</td>
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<td>7.565</td>
<td>10.113</td>
<td>-</td>
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<td>50.40</td>
<td>0.081</td>
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<td>-0.835</td>
<td>29.1</td>
<td>2.80</td>
<td>7.374</td>
<td>8.432</td>
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<td>8.244</td>
<td>9.605</td>
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<td>61.72</td>
<td>0.054</td>
<td>18.3</td>
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<tr>
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<td>23.6</td>
<td>2.32</td>
<td>7.640</td>
<td>10.124</td>
<td>28.0</td>
<td>71.74</td>
<td>0.052</td>
<td>29.7</td>
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</tr>
<tr>
<td>20</td>
<td>-0.861</td>
<td>22.9</td>
<td>2.10</td>
<td>8.036</td>
<td>9.393</td>
<td>30.18</td>
<td>78.16</td>
<td>0.049</td>
<td>30.15</td>
<td></td>
</tr>
</tbody>
</table>
AC impedance method

AC impedance Nyquist plots for zinc in the presence and absence of inhibitor at different temperature as shown in Fig.3. An equivalent circuit model (Fig.4.) was used to fit the Nyquist plots. The parameters such as polarization resistance \( R_p \) and double capacitance values \( (c_{dl}) \) are measured using equivalent circuit are listed in Table.1. Inhibition efficiency \( (\eta_z) \) was calculated using the following equation.

\[
\eta_z = \frac{R_p - R_p^o}{R_p} \times 100
\]

where \( R_p^o \) and \( R_p \) are the polarization resistances for uninhibited and inhibited solutions, respectively.

The depressed semicircle shows the characteristics for solid electrodes and it is referred to as frequency dispersion. This frequency dispersion is attributed to roughness and inhomogeneities [17]. According to many literatures [18, 19, 20], two models have been adopted to describe the EIS spectra for the inhomogeneous films on the metal surface of rough and porous electrodes. One is the filmed equivalent circuit model and the other is the finite transmission line model. In this work, the filmed equivalent circuit model is used to describe the inhibitor-covered metal/solution\interface [21].
Adsorption isotherm and Thermodynamic considerations
The interaction between the inhibitor and the metal surface can be explained by the adsorption isotherm, which depends on the degree of electrode surface coverage (θ). The most frequently used isotherms are Langmuir, Frumkin, Bockris-Swinkel, El Awardy, Flory Huggins and Temkin adsorption isotherms [22].

In the present work, the investigator applied Freundlich adsorption isotherm, Temkin
adsorption isotherm and the Langmuir adsorption isotherm at 303K -333K. The plot of C/θ against C with the regression coefficient nearly equal to 1.0 which suggests the adsorption of the compound on the metal surface followed the Langmuir adsorption isotherm model at all temperatures, figure 5.

Fig.5. A) Freundlich adsorption isotherm C) Temkin adsorption isotherm B) Langmuir adsorption isotherm at 303K -333K.
Table 2. Thermodynamic Parameters for zinc in 0.1M HCl in the absence and presence of different ketosulfone concentrations.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>K_{ads} (M^{-1})</th>
<th>G^0_{ads}(kJ mol^{-1})</th>
<th>H^0_{ads} (kJ mol^{-1})</th>
<th>S^0_{ads} (J mol^{-1} K^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>259067.35</td>
<td>-12.6</td>
<td>-25.19</td>
<td>-41.5</td>
</tr>
<tr>
<td>313</td>
<td>232558.13</td>
<td>-12.9</td>
<td>-25.19</td>
<td>-39.2</td>
</tr>
<tr>
<td>323</td>
<td>18867.92</td>
<td>-10.61</td>
<td>-25.19</td>
<td>-45.1</td>
</tr>
<tr>
<td>333</td>
<td>17011.0</td>
<td>-10.83</td>
<td>-25.19</td>
<td>-43.1</td>
</tr>
</tbody>
</table>

Fig. 6. Relationship between \(-\Delta G^0_{ads}/T\) v/s 1000/T

According to Langmuir adsorption isotherm, \(\theta\) is related to equilibrium adsorption constant \((K_{ads})\) and \(C\) by the equation:

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

(1)

Where \(C\) is the concentration of inhibitor and \(K\) is the equilibrium constant. The strong adsorption of inhibitor on the zinc surface obeys Langmuir’s adsorption isotherm. The \(K_{ads}\) values were calculated from straight line intercept obtained from the plot of \(C/\theta\) versus \(C\). This is related to the standard free energy of adsorption (\(G^0_{ads}\)) with the following equation.
\[ K_{ads} = \frac{1}{55.5} \exp \left( -\Delta G^0_{ads}/RT \right) \]  

(2)

The gas constant is donated by R and absolute temperature is donated by T. The obtained results \((K_{ads} \text{ and } \Delta G^0_{ads})\) are depicted in the Table.2.

The \(\Delta H^0_{ads} \text{ and } \Delta S^0_{ads}\) are also calculated from the Gibbs-Helmholtz equation. The Gibbs-Helmoltz equation can be written as [23],

\[
\left\{ \frac{\partial (\Delta G^0_{ads}/T)}{\partial T} \right\}^p = \frac{-\Delta H^0_{ads}}{T^2}
\]

By integrating the above equation, we get

\[
\frac{\Delta G^0_{ads}}{T} = \frac{\Delta H^0_{ads}}{T} + K
\]

(4)

The relationship between \(\Delta G^0_{ads}/T \text{ V/S 1000/T}\) depicted in Fig.6, with the slope equal to the \(\Delta H^0_{ads} \text{ and } \Delta S^0_{ads}\) is the intercept. \(\Delta H^0_{ads} \text{ and } \Delta S^0_{ads}\) are reported in the table 2.

In the present study the \(\Delta G^0_{ads}\) carries a negative sign which indicates that the adsorption process occurs spontaneously and explains the adsorbed layer of inhibitor on the metal surface is stable [24]. The Many literatures reported physisorption, when the magnitude of \(\Delta G^0_{ads}\) around \(\sim -20 \text{ KJ/mol}\) or less and those approaches to \(\sim -40 \text{ kJ/mol}\) are indicative of chemisorption. In the present study investigator obtained the maximum value of \(-12.8 \text{ KJ/Mol}\) and it is concluded that the inhibitor adsorption on the metal surface follows physisorption [25].

**Activation parameters:**

The rate of corrosion increases with increase in the temperature. The effect of temperature on the mechanism of corrosion and corrosion inhibition can be explained by the activation parameters. The effect of temperature on corrosion and corrosion inhibition is studied using Arrhenius equation and Transition state plots [26].

The Arrhenius equation can be written as,

\[
\ln v_{corr} = \ln A - \frac{E_a^*}{RT}
\]

(9)

Where \(v_{corr}\) is the corrosion rate, \(E_a^*\) is the apparent activation energy (J/mol), \(R\) is the gas
constant (8.314 J/mol/K), $T$ is the absolute temperature (K) and $A$ is the Arrhenius pre-exponential factor. Fig. 7 presents the Arrhenius plot of $\ln \nu_{corr}$ against $1/T$ for the corrosion of mild steel in 1M HCl solution in the presence and absence of inhibitor. From Fig. 6, the slope ($-E_a^*/R$) of each individual straight line was determined and the apparent activation energy ($E_a^*$) was calculated using the expression $E_a^* = \text{slope} \times R$ (8.314 J/mol/K). The calculated apparent activation energy ($E_a^*$) values and Arrhenius pre-exponential factors can be reported in Table 3.

![Fig.7. Arrehnious plot](image-url)
Table 3. Activation Parameters for zinc in 0.1M HCl in the absence and presence of different ketosulfone concentrations.

<table>
<thead>
<tr>
<th>Concentration of Inhibitor (ppm)</th>
<th>$E_a^*$ (kJ/mol)</th>
<th>$A$ (kJ mol$^{-1}$)</th>
<th>$H^*$ (kJ mol$^{-1}$)</th>
<th>$S^*$ (J mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td>5</td>
<td>14.00</td>
<td>441.42</td>
<td>-28.5</td>
<td>-16.83</td>
</tr>
<tr>
<td>10</td>
<td>15.63</td>
<td>685.39</td>
<td>-30.0</td>
<td>-17.55</td>
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<tr>
<td>15</td>
<td>16.43</td>
<td>854.05</td>
<td>-30.3</td>
<td>-17.68</td>
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<tr>
<td>20</td>
<td>20.11</td>
<td>3084.3</td>
<td>-32.0</td>
<td>-18.82</td>
</tr>
</tbody>
</table>

The values of the standard enthalpy ($\Delta H^*$) and standard entropy ($\Delta S^*$) of activation were calculated by the following equation [27]

$$\frac{\ln(\frac{\eta_{\text{corr}}}{T})}{T} = \left[ \ln \left( \frac{R}{N_h} \right) + \frac{\Delta S^*}{R} \right] - \frac{\Delta H^*}{R} \quad (10)$$

Where $h$ is plank’s constant ($6.626 \times 10^{-34}$ m$^2$kg/s) and Avogadro’s number ($6.022 \times 10^{23}$).

A Transition plot of $\ln(\frac{\eta_{\text{corr}}}{T})$ Vs $1/T$ gave straight lines (Fig.8) and are depicted in Table.3.
ΔH* value calculated by using slope with an expression. \( \Delta H^* = \text{slope} \times R \times (8.314) \) and \( \Delta S^* \) calculated by the help of intercept with an expression \( \Delta S^* = \text{intercept} - \ln \frac{B}{Nk} \). The calculated values of \( \Delta H^* \) and \( \Delta S^* \) are listed in Table 3.

The inhibition efficiency of Ketosulfone decreases with temperature and this results in the increase in the apparent activation corrosion energy. This trend probably was attributed to physiortion of Ketosulfone on the zinc surface [28].

The positive signs of enthalpies (\( \Delta H^* \)) show that the dissolution process is endothermic in nature. The shift towards positive value of entropies (\( \Delta S^* \)) implies that the increasing in the disorderliness of reactants to the activated complex [29, 30].

**Scanning Electron spectroscopy**

The surface appearance of the zinc in 0.1M HCl solution in the absence and in the presence of ketosulfone inhibitor by using Scanning Electron Microscopy (SEM) are shown in figure 9.

When a smooth surface of zinc is immersed in 0.1M HCl for 8 hrs, A corroded surface is observed in the SEM image. However, in the presence of inhibitor, the surface improved markedly in terms of smoothness. Usually a protective film coated on the mild steel surface, which proceeds to a considerable reduction of the corrosion process.

A.

B.
3. Experimental

Material

The corrosion inhibition studies were carried out for Zinc samples of pure grade (Cu 0.17%, Ti 0.075%, Al <0.05%, Pb - Cd <0.003%, Fe 0.002%, Sn 0.001% and Mg 0.0005% remaining is Zn). Electrochemical measurements carried out for the strips with an exposed area of 1 cm². The samples were polished by emery paper (Grade No.: 80-1500), washed thoroughly with distilled water.

4. Methodology

Tafel Polarization method and AC-impedance method

The Ivium electrochemical analyzer is used to carry out the Tafel Polarization method and AC-impedance method at 303-333K. The cell consists of working electrode (zinc), indicator electrode (PT electrode) and secondary reference electrode (Calomel electrode). Before each electrochemical measurement, steady state open circuit potential (OCP) is noted down.

In Tafel Polarization measurements, Tafel curves (Log current Vs Potential) were recorded at a scan rate of 0.001 V s⁻¹ in the potential range of -0.2 and +0.2 V.

In AC-Impedance measurements, Nyquist plots were recorded at the amplitude of 5 mV in the
frequency range from 100 KHz to 10 MHz. An appropriate equivalent circuit is used to fit the Nyquist plots by using Z-Simp Win 3.21 software.

**Adsorption Isotherm and thermodynamic parameters:**
The mode of adsorption of Ketosulfone on zinc in 0.1M HCl at different temperature studied by adsorption isotherms like Freundlich adsorption isotherm, Temkin adsorption isotherm and Langmuir adsorption isotherm at 303K -333K. Thermodynamic parameters were calculated by using graphs.

**Scanning electron microscopic (SEM) studies**
Zinc strip with dimensions of 1.0 cm x 1.0 cm x 0.1 cm were abraded with emery papers from grade no. 80 up to 1200, cleaned with double distilled water, rinsed with acetone and dried at room temperature. After immersion in 0.1M HCl in the absence and presence of the optimum concentration of inhibitor at 25°C temperature for 4 hours. The zinc strip was again rinsed with distilled water and acetone dried at room temperature. Then SEM images were recorded using the JEOL JSM-840A model. The energy of the accelerating beam employed was 20 V.

**5. Conclusions**
- There is a good agreement between polarization method and Ac-impedance method at 303-333K.
- The maximum % I.E. of Ketosulfone for the zinc metal in acidic media is 59.09%.
- % I.E. deceases after 313K.
- Tafel plots reveal the Ketosulfone is a mixed type inhibitor.
- Adsorption of the inhibitor follows the Langmuir isotherm.
- The interaction of inhibitor on the zinc surface takes place through physical adsorption.
- Activation parameters explain the corrosion process.
- A small amount of inhibitor shows inhibition efficiency.

**6. Acknowledgements**
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