Amino acid Schiff bases as efficient corrosion inhibitor for mild steel in aqueous H$_2$SO$_4$: a comparative study

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**Abstract** — Corrosion inhibitory performance of two Schiff bases prepared through condensation of two different amino acids, glycine and tyrosine with a common aldehyde, citronellal (designated as GCSB and TCSB, respectively) are compared by taking mild steel as test metal and aqueous H$_2$SO$_4$ as the corrosive environment. Inhibition efficiencies as obtained through potentiodynamic polarization and electrochemical impedance spectroscopic methods establish TCSB as a superior corrosion inhibitor with 74 to 88 percentage of inhibition efficiency. Better corrosion mitigatory prowess of TCSB is explained in terms of various intrinsic molecular parameters, like the energy of frontier molecular orbitals (HOMO and LUMO), global hardness, softness, electrophilicity index, and others. It is revealed that two directional electron transfer, inhibitor to metal and retro-transfer, is responsible for the interaction of the Schiff bases with the metal surface. From electron distribution at HOMO and LUMO levels, atoms or functional groups present in the Schiff bases which initiate the molecular interaction with metal surface are ascertained.

**Keywords** — mild steel, amino acid Schiff base, Corrosion inhibition, EIS, DFT

1. INTRODUCTION

All forms of corrosion of metal and alloy are detrimental and incur huge economic loss (ranged from about 2-5% of the gross national product) [1]. With growing economic activities, problem associated to corrosion is becoming more and more severe. Combating corrosion in an effective and economic way is of utmost importance now-a-days. Various methods available to address the problem include application of coating, cathodic protection, change in design and use of suitable inorganic or organic inhibitors [2]. Due to toxicity and adverse environmental effect, use of different inorganic corrosion inhibitors, particularly those based on chromates, tungstates, molybdates, phosphates and arsenic compounds, is being gradually restricted by regulatory bodies [3]. This leaves the use of organic corrosion inhibitors, which are relative benign towards environment as the only viable alternative. Among several classes of organic corrosion inhibitor, use of heterocyclic organic bases has some unique advantages [4,5]. Lone pair of electrons present on the heteroatom as well as unsaturated bonds present can interact with the metal surface. Planarity of these bases has

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resulted in greater and more efficient surface coverage. Moreover, these are soluble in acidic medium. High degree of inhibition efficiency for a prolonged period of exposure time has made them very suitable candidate as corrosion inhibitor. Above all, these are being incorporated in the formulation of anti-fouling coating system due to their anti-bacterial and anti-fungal effect.

Investigating the structure-reactivity relationship is a key component to understand the whole process of adsorption of inhibitors on the metal surface and subsequent inhibition of corrosion of the later. By these studies, several important conclusions have been drawn regarding the effectiveness of a corrosion inhibitor. Influence exerted by the heteroatoms present in an inhibitor is expected to vary in the order P>S>N>O [6]. Moreover, quantum chemical calculations (DFT calculations) have revealed that for structurally comparable corrosion inhibitors, inhibition efficiency is higher for the one having least energy gap between the frontier molecular orbitals (HOMO and LUMO). Other intrinsic molecular parameters, like polarity of the molecule (dipole moment value), global hardness and softness and others play specific role towards dictating the extent of interaction between the inhibitor molecule and the metal surface [7]. In fact, analysis of electron distribution in HOMO and LUMO energy levels helps to ascertain the atom or group present in the inhibitor susceptible for electron donation to the metal surface and electron acceptance (back bonding) during adsorption.

In addition of the all these factors, it is demonstrated by our group that stereochemical configuration of the inhibitor is an important factor to guiding the extent of adsorption and corrosion inhibition.

In the present study, we have prepared two different Schiff bases by condensing different amino acids, glycine or tyrosine with citronellal, as naturally occurring aldehyde (GCSB and TCSB, Fig. 1). Citronellal, a monoterpenoid aldehyde, is extracted from lemongrass [8]. Combination of amino acid and naturally occurring aldehyde is expected to be environmentally sustainable, as both precursor molecules are derived from bio resources. While glycine is the simplest amino acid, tyrosine contains an additional phenolic group in its structure. Citronellal, on the other hand, possesses aliphatic C-chain along with one C=C bond. In addition, formation of Schiff base results into an unsaturated imine bond. It is expected to be interesting to explore the effect of variety of functional groups, hydrophilic C-chain, pi-electron cloud of C=C and C=N bonds on the overall corrosion inhibitory performance of the studied Schiff bases [9].

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Figure 1 - Chemical Structure of the studied amino acid Schiff bases

2. EXPERIMENTAL

A. Preparation and characterization of Schiff bases
Schiff bases are synthesized by conventional method, where the amino acid (glycine or tyrosine) is refluxed with citronellal (1:1 mole ratio) in methanol under slightly basic condition (Scheme 1). Methanol is evaporated, and the product is washed with ether.

FTIR spectra of citronellal, GCSB and TCSB are shown in Fig. 2. Band at 1721 cm\(^{-1}\) in citronellal corresponds to the aldehyde group. This band is absent in the corresponding spectrum of the Schiff bases. New band (or hump) in the range 1653 to 1684 cm\(^{-1}\) designates formation of imine band (C=N) characteristics of Schiff bases [7,9].

![Scheme 1- Synthetic route for preparation of the studied Schiff bases](image-url)

B. Potentiodynamic Polarization

Potentiodynamic polarization studies will be carried out to measure the corrosion rate and inhibition efficiency in a conventional 3 electrode system (metal as a working electrode, Pt mess as an auxiliary electrode and calomel as the reference). This will further ascertain if the
inhibitor be anodic, cathodic or mixed type in nature. Inhibition efficiency of the inhibitor, $\eta_p(\%)$ is defined as:

$$\eta_p(\%) = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \times 100$$

where, $i_{corr}$ and $i_{corr(inh)}$ are the values of corrosion current density of uninhibited and inhibited specimens, respectively.

**C. Electrochemical Impedance Spectroscopy (EIS)**

It will be used in characterizing the adsorption and anti-corrosive behaviour of inhibitors at metal surface by determining polarization resistance ($R_p$) and electrochemical mechanism. Polarization resistance relates directly to the degree of surface coverage of inhibitor molecules on metal surface and in-turn inversely related to corrosion rate. EIS study will tell if the corrosion process at the metal-solution interface is simply charge-transfer controlled or diffusion controlled. Determination of polarization resistance as a function of time will provide information regarding the dynamics of adsorption process. Inhibition efficiency in terms of $R_p$, $\eta_Z(\%)$ is defined as:

$$\eta_Z(\%) = \frac{R_p - R_p^0}{R_p} \times 100$$

where, $R_p$ and $R_p^0$ are the values of polarization resistance in presence and absence of the inhibitor.

**D. DFT Calculation**

Following Koopmans’ theorem, different intrinsic molecular quantities like electronegativity ($\chi$, a measure of the power of a group of atoms to attract electrons towards itself), global hardness ($\eta$, a parameter related to the resistance of an atom to a charge transfer) and global softness ($\sigma$, which shows the reactivity of the inhibitor molecules in terms of charge transfer), etc., which are supposed to influence the overall reaction between two interacting systems, have been calculated [10,11]. These quantities are related to electron affinity (A) and ionization potential (I) as follows (eqs. 3-7):

$$\chi = (I+A)/2$$

$$(3)$$

$$\eta = (I-A)/2$$

$$(4)$$

$$\sigma = 1/\eta = 2/(I-A)$$

$$(5)$$

$I = -E_{HOMO}$

$$(6)$$

$A= -E_{LUMO}$

$$(7)$$

From these values, the fraction of electrons transferred from the inhibitor molecule to the metallic atom (AN) is obtained using the following relation [10,11]:

$$\Delta N = \frac{(\chi_{Fe} - \chi_{inh})}{2(\eta_{Fe} + \eta_{inh})}$$

$$(8)$$

As per its underlying concept, during the reaction of two systems having different electronegativities (here, the metallic surface and an inhibitor molecule) the following
mechanism will take place: the electron flow will happen from the molecule with lower electronegativity towards that of a higher value, until the chemical potentials become the same.

Energies of HOMO and LUMO and energy gap between these levels are directly related to electron donation and acceptance property of the molecule. This, in-turn guides the extent or magnitude of any molecular interaction. From the electronic distribution in HOMO and LUMO, atom or group, present in the inhibitor system, responsible for electron donation or acceptance can be ascertained.

3. RESULTS AND DISCUSSION

A. Electrochemical impedance spectroscopy (EIS) results

Nyquist plots for mild steel in 0.5 M H₂SO₄ in absence and presence of amino acid Schiff bases are shown in Fig. 3. In all cases, a single capacitive loop is observed in the Nyquist plots, which suggests one time-constant associated with the charge transfer processes at the metal-electrolyte interface. Diameter of the capacitive loop increases with inhibitor concentration, indicating higher resistance towards charge transfer offered by the inhibitor molecules at higher concentration. This manifests enhanced degree of surface coverage by inhibitor molecules when concentration is at higher side. Following these observations, Nyquist plots are fitted with an electrical equivalent circuit, as depicted in Fig. 4. In this equivalent circuit, constant phase element (CPE) is introduced, in stead of double layer capacitance (C_{dl}) to accommodate the depressed nature of the capacitive loop under the real axis. This is very common phenomena for a non-ideal surface, which is heterogeneous in nature, both chemically and physically [12]. Impedance of CPE is given as:

$$Z_{\text{CPE}} = Q^{-1} (i\omega)^{n}$$  (9)
where, \( Q \) and \( n \) are two fitting parameters. The CPE reduces to a resistor for \( n = 0 \), to a Warburg element for \( n = 0.5 \) and to an ideal capacitor for \( n = 1 \) (for a homogeneous surface). \( R_p \) is the charge transfer resistance. From table 1, it is revealed that \( R_p \) is higher for TCSB than that for GCSB at all concentrations. Inhibition efficiency calculated from \( R_p \) values establishes TCSB as better corrosion inhibitor, as it imparts 83% inhibition efficiency at 2 mM concentration over 70% inhibition efficiency for GCSB at same concentration.

### Table 1 - EIS data for mild steel in 0.5 M H\(_2\)SO\(_4\) in presence and absence of amino acid Schiff bases

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Conc (mM)</th>
<th>( R_p ) (Ω cm(^2))</th>
<th>Q (µΩ(^{-1}) s(^n) cm(^{-2}))</th>
<th>( \eta_z ) (%)</th>
<th>( \chi^2 \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uninhibited</td>
<td>8.8</td>
<td>224</td>
<td>0.86</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>GCSB</td>
<td>1</td>
<td>26.1</td>
<td>73</td>
<td>0.86</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>30.2</td>
<td>71</td>
<td>0.84</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>33.8</td>
<td>54</td>
<td>0.84</td>
<td>74</td>
</tr>
<tr>
<td>TCSB</td>
<td>1</td>
<td>27.5</td>
<td>67</td>
<td>0.89</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>54.5</td>
<td>119</td>
<td>0.86</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>73.7</td>
<td>85</td>
<td>0.84</td>
<td>88</td>
</tr>
</tbody>
</table>

### B. Potentiodynamic polarization study

Potentiodynamic polarization plots for mild steel in 0.5 M H\(_2\)SO\(_4\) without and with different concentrations of GCSB and TCSB are depicted in Fig. 5. Corrosion parameters obtained after fitting the plots by Tafel extrapolation method are tabulated in table 2. In the presence of GCSB and TCSB, the anodic and cathodic current densities decrease over the whole potential range compared to those for uninhibited sample. This exemplifies the amino acid Schiff bases as mixed type inhibitors, where those cathodic and anodic reaction sites are being blocked by the inhibitor molecules, and thereby retarding the rate of corresponding reactions. Mixed type corrosion inhibition property is also manifested from the change in corrosion potential values in the presence of inhibitors, which does not vary to any appreciable extent with respect to that in the absence of any inhibitor [13]. Inhibition efficiency as obtained from corrosion current values also supports the conclusion as derived from EIS study, that TCSB is a better corrosion inhibitor than GCSB for mild steel in 0.5 M H\(_2\)SO\(_4\). It seems the presence of additional phenolic group is bestowing TCSB some extra potentiality to get adsorbed on the metal surface and thereby enhanced corrosion mitigation propensity.
Figure 5 - Potentiodynamic polarization plots for mild steel in 0.5 M H₂SO₄ in presence and absence of amino acid Schiff bases

Table 2 - Corrosion parameters as determined from potentiodynamic polarization plots

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Conc (mM)</th>
<th>-E_corr (mV/SCE)</th>
<th>b_a (mV/dec)</th>
<th>-b_c (mV/dec)</th>
<th>i_corr (mA/cm²)</th>
<th>η_p (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uninhibited</td>
<td></td>
<td>470</td>
<td>174</td>
<td>212</td>
<td>3.24</td>
<td></td>
</tr>
<tr>
<td>GCSB</td>
<td>1</td>
<td>470</td>
<td>102</td>
<td>186</td>
<td>1.20</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>470</td>
<td>104</td>
<td>153</td>
<td>1.09</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>471</td>
<td>98</td>
<td>160</td>
<td>1.02</td>
<td>68</td>
</tr>
<tr>
<td>TCSB</td>
<td>1</td>
<td>455</td>
<td>115</td>
<td>144</td>
<td>0.98</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>452</td>
<td>103</td>
<td>158</td>
<td>0.93</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>470</td>
<td>95</td>
<td>113</td>
<td>0.89</td>
<td>73</td>
</tr>
</tbody>
</table>

C. Result from density functional theory (DFT) calculation

DFT calculation returns various intrinsic molecular parameters, which are tabulated in table 3. Higher HOMO energy implies easier electron transfer from HOMO of inhibitor to the vacant 3d orbitals of Fe. Similarly, lower LUMO energy facilitates retro-electron transfer, i.e. from filled 4s electrons from Fe to the LUMO of the inhibitor molecule. Combining these two processes, we may argue that lower energy gap between HOMO and LUMO of inhibitor molecules corresponds to better inhibitor-metal interaction in terms of both way electron transfer [14]. Among the studied amino acid Schiff bases, TCSB has higher HOMO and lower LUMO energies. This suggests TCSB is energetically more favorable to interact with the metal surface by virtue of more facile electron donation as well as acceptance. This is also reflected when we compare the values of global softness for TCSB and GCSB. TCSB has higher global softness value, which reiterates better molecular interaction (mostly van der Walls interaction) of capability of TCSB with any other chemical species than GCSB. If we focus into electrophilicity index and electronegativity values, TCSB is ahead of GCSB. This reflects better electron acceptance power of TCSB over GCSB. Hence, TCSB is better in accepting electron from the metal surface. This makes fraction of electron transferred from inhibitor to metal (ΔN_{110}) value lesser for TCSB. Thus, overall extent of adsorption of
inhibitors, on which corrosion inhibition efficiency depends, is guided by both electron donation well as acceptance [15].

Electron density distribution in HOMO and LUMO is quite different for two inhibitors (Fig. 6). This dictates the difference in the mode of adsorption for the two studied inhibitor molecules. In GCSB, electron density in HOMO is over the C=C bond of the citronellal unit. In TCSB, electron density, in addition to the C=C bond of citronellal unit, is distributed also on the phenolic moiety of the tyrosine unit. Thus, more number of functional groups is available for electron donation to the metal for TCSB than GCSB. LUMO electron density in

Table 3 - Electronic and calculated intrinsic molecular parameters for studied inhibitors

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>$I$ (eV)</th>
<th>$A$ (eV)</th>
<th>$\chi$ (eV)</th>
<th>$\eta$ (eV)</th>
<th>$\sigma$ (eV$^{-1}$)</th>
<th>$\omega$ (eV)</th>
<th>$\Delta N_{110}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCSB</td>
<td>-6.3088</td>
<td>-0.4044</td>
<td>5.904</td>
<td>6.309</td>
<td>0.404</td>
<td>3.357</td>
<td>2.952</td>
<td>0.339</td>
<td>0.954</td>
<td>2.16</td>
</tr>
<tr>
<td>TCSB</td>
<td>-6.2186</td>
<td>-0.7923</td>
<td>5.426</td>
<td>6.219</td>
<td>0.792</td>
<td>3.505</td>
<td>2.713</td>
<td>0.368</td>
<td>1.132</td>
<td>1.783</td>
</tr>
</tbody>
</table>

Table 3 - Electronic and calculated intrinsic molecular parameters for studied inhibitors

![Figure 6 - Electronic distribution of electron density in HOMO and LUMO levels for studied inhibitors](image-url)
GCSB is distributed mostly on the imine bond and the carboxylic group. For LUMO in TCSB, in addition to the groups as observed for GCSB, electron density is also delocalized on the phenyl ring of tyrosine moiety to some extent. Thus, for TCSB, more functional groups are available for electron acceptance from the metal, just like electron donation. Hence, TCSB interacts with the metal surface with greater percentage of molecular surface, compared to GCSB. Mild steel surface will thus be covered more effectively with TCSB than with GCSB at same concentration level. In accordance to the above discussion, the mode of adsorption of TCSB on mild steel surface is illustrated schematically in Scheme 2.

![Scheme 2](image.png)

Scheme 2 - Possible mode of interaction of TCSB with mild steel surface as enumerated from DFT calculation

4. CONCLUSION

Amino acid Schiff bases exert considerable amount of corrosion inhibition for mild steel in aqueous H$_2$SO$_4$ medium. Extent of inhibition efficiency depends on the presence of functional groups present in the amino acid backbone. Schiff base derived from citronellal and tyrosine is superior corrosion inhibitor than that derived from citronellal and glycine. It is seen that the presence of phenolic group in tyrosine is providing better opportunity for electron donation as well as acceptance. Amino acid Schiff bases act essentially as mixed type corrosion inhibitor. Inhibition efficiency trend is explained in terms of energies of the frontier molecular orbitals and other intrinsic molecular parameters.

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References


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