Benzylidene Schiff base Corrosion Inhibition and Electrochemical Studies of Mild Steel In 1M HCl and 0.5m H₂SO₄ acidic Solutions

K. SENTHIL MURUGAN¹ and T. MOHANAPRIYA²*

¹,²Department of Chemistry, Erode Arts and Science College (Autonomous), Erode, Tamilnadu, 638 009, India.
²*Corresponding author E-mail: mohanapriyachem@gmail.com

http://dx.doi.org/10.13005/ojc/380512

(Received: September 10, 2022; Accepted: October 11, 2022)

ABSTRACT

N-Benzylidene-4-Methoxyaniline (NB4MA) Schiff base was synthesized and investigated corrosion behavior of mild steel (MS) in 1M HCl and 0.5M H₂SO₄. The corrosion efficiency studied by means of mass loss and electrochemical techniques. The electrochemical studies confirm that Ecorr displacement about 32mV confirms anodic and cathodic type of inhibitor. The positive direction of corrosion potential curves confirmed that adsorption efficiency on metal surface. Langmuir adsorption isotherm was observed. Electrochemical impedance studies (EIS) exposed that inhibition effectiveness enlarged with even increasing concentration of Schiff base and found inhibition capacity 90-95%. Furthermore, thermodynamic parameters of adsorption were found which elaborates that increasing ΔG°ads parameter since favorable interaction behavior between mild steel and inhibitor causes efficient adsorption. The morphology studies revealed that synthesized Schiff base has strong affinity to adhere on mild steel and improve corrosion efficiency against acidic media. The quantum chemical parameter also confirmed that electrons distribution and efficiency of Schiff base.

Keywords: Corrosion, Inhibition, Schiff base, Impedance studies, Quantum chemical parameter.

INTRODUCTION

Metal corrosion process happens frequently which mainly ensue and directly affect the industrial equipment. The mild steel is extensively utilized for build materials reason in many industries such as petroleum production industry, power generation plants and cooling tower. Normally, Hydrochloric acid and sulphuric acid solutions specifically has been used for cleaning purpose when acidizing functions cause possibility to happen corrosion in the steel. The inhibitor used to protect corrosion for that intention prepare organic compound contains hetero atoms utilized for excellent corrosion inhibitor of steel present in acidic media. The inhibitor is adsorbed on metal surface by the means of the electron donating N, S, P and O atoms as well as double/ triple bonds or aromatic ring¹.

Recently, derivatives of Benzylidene amine Schiff base molecules expressed by the formula C₆H₅.CH=N-C₆H₅ are considered a significant
inhibitor behavior because of presence azomethine group –CH=N and aromatic ring pi-electron. These molecules are thin hence their products are reducing rate of corrosion since slowing anodic reaction\(^2\). Ece Altunbas Sahin \textit{et al.},\(^3\) reported that corrosion effect in 1 N HCl of using synthesized 4 amino N-benzylidene-benzamide Schiff base suggested that Langmuir adsorption isotherm for adsorption process and protective film was formed homogeneously on the metal steel develops inhibition capacity due to presence of amine and aldehydes involving in inhibition action.

El Hassane Anouar \textit{et al.},\(^4\) investigated that substituted benzidine Schiff base corrosion effect on mild steel immersed in 1M HCl. It suggested that benzene ring C=C and C=N involving in chemisorptions pi-pi interaction and suggested functional group C=O and C=N and heteroatom O, N, S increasing protecting ability of inhibitors is strengthen by molecular structure such as electro negativity of hetero atom and aromatic electron clouds. M. A. Bedair reported benzidine based Schiff base compound inhibition efficiency found in carbon steel of 1.0M HCl further concludes that benzidine derivative efficient corrosion inhibition followed chemisorptions, Langmuir adsorption especially aromatic ring, imine group and lone pair electron of hetero atoms leads inhibition efficiency. Abdelghani Madani \textit{et al.},\(^6\) Suggested that synthesis of benzidine based Schiff base and demonstrated from SEM and DFT quantum studies that function groups are responsible for corrosion inhibition performance. Corrosion inhibition sites such as hetero atom, aromatic ring, azomethine linkage group are inevitable groups those contribute major role for the purpose of adsorption between metal surfaces and inhibitor then improves efficiency of inhibitor in acidic solution 1.0 N HCl along with mild steel.

Recently, Caio Machado Fernandes \textit{et al.},\(^7\) reported that mild steel present in HCl using green synthesized benzylidene derivative as inhibitor and suggested that electrochemical behavior indicates corrosion process increasing due to reducing anodic and cathodic corrosion reaction. AFM, SEM depicted smooth surface in the presence of organic molecules due to formation of protective layer, covalent bond formation with steel act as corrosion inhibition confirmed by DFTB. Hulya Keles \textit{et al.},\(^8\) reported that benzylidene compound inhibition behavior in 1M HCl which exposed that the immersion time extends corrosion inhibition, hetero atom and aromatic ring pi-electrons were found the possible interaction site on the inhibition surface.

In this study, synthesized a Schiff base N-benzylidene-4-methoxyaniline by using precursor p-anisidine and benzaldehyde. Especially, chosen for above Schiff base since presence of –CH=N– and –OCH\(_3\) these groups consist donor hetero atoms induces adhere metal surface of mild steel creates effective corrosion inhibition efficiency. Further the synthesized inhibitor corrosion effectiveness on mild steel surface has been investigated in the presence of acidic solutions 1M HCl and 0.5M H\(_2\)SO\(_4\). The corrosion effect has been examined by the means of weight loss method, polarization plots, electrochemical impedance study, scanning electron microscope (SEM). The density functional theory (DFT) at B3LYP/6-31G level has been used to determined quantum chemical calculation of the inhibitor molecules.

**MATERIALS AND METHODS**

p-anisidine [4-(CH\(_3\)O) C\(_6\)H\(_4\)NH\(_2\) (assay 98%)], benzaldehyde [C\(_6\)H\(_5\)CHO (assay 99%)], ethanol [Assay 99.9%]. 1 M HCl (assay 37%) and 0.5M H\(_2\)SO\(_4\) (95-97%) chemicals were purchased from Merck. Then 1 M Hydrochloric acid, 0.5M H\(_2\)SO\(_4\) solutions were prepared by using distilled water.

**Synthesis and Characterization**

The Schiff base N-Benzylidene-4-Methoxy aniline was synthesized by adding p-anisidine and benzaldehyde are dissolved in minimum amount of ethanolic solution followed a round bottom flask used to mix above solutions. Then refluxed 45°C maintained six hours finally transfer into ice cold water, grey color crystals separated out. This solid product was recrystallized with ethanol. The above synthesized crystalline corrosion inhibitor (melting point 112°C)\(^9\) denoted as NB4MA.

Mild steel has been used for examine corrosion effectiveness denoted MS. The reaction scheme is shown in Figure 1.

**Weight loss method**

Corrosion inhibition efficiency found using following equation,

\[
\text{Inhibition efficiency (}\eta\text{)} = \frac{W_0 - W}{W_0}
\]
Where, W0-MS weight loss without inhibitor, W-weight loss of MS by means of synthesized inhibitor. The various concentration of Schiff base inhibitor was used to examine inhibition efficiency of MS in acidic solutions.

\[
\text{Inhibition efficiency (}\eta_{\text{pol}}\text{)} = \frac{I_{\text{corr}}^0 - I_{\text{corr}}'}{I_{\text{corr}}^0}
\]

Where, corrosion current densities \(I_{\text{corr}}^0\) and \(I_{\text{corr}}'\) were blank and presence of inhibitors respectively. The adsorption isotherm has been used to calculate surface coverage (\(\theta\)) which can be calculated following equation\(^{11}\).

\[
\theta = \frac{\eta_{\text{pol}}}{100}
\]

**Quantum chemical calculation methods**

Density functional theory (DFT) was applied calculate HOMO- LUMO, Electro negativity (\(\chi\)), and other quantum chemical parameter values in level basis set B3LYP and 6-31G. Gaussian 09W software has been used to conclude the molecule geometry and structure optimization of prepared Schiff base NB4MA inhibitor.

**RESULTS AND DISCUSSION**

The formation of Schiff base N-Benzylidene-4-Methoxyaniline has been confirmed by following spectroscopic studies and shown in Figure 2, 3 and 4.
Corrosion inhibition efficiency was increased with inhibitor concentration and found 93.1% and 89.8% for 1M HCl and 0.5M H₂SO₄ correspondingly. The molecules displayed efficiency on mild steel because of presence of –C=N group and hetero atom attached. Moreover, the azomethine linkage and aromatic ring increases inhibition efficiency at room temperature. The metal surface has been protected since inhibitor was adsorbed causes protective layer formed on the surface of MS corrosion prevention occurs. The concentration of inhibitor increased with inhibition efficiency.

### Electrochemical parameter

Potentiodynamic polarization studies were done by Tafel extrapolation shown in Fig. 6. It is useful to determination of corrosion potential (E₉₀Ο), corrosion current density (I₉₀Ο) and inhibition efficiency (ηpol%). Tafel data is one of polarization studies in between -0.2 to -0.8V with sweep rate of 1 mV/s. The acidic solutions 1M HCl and 0.5M H₂SO₄ inhibition effectiveness found to be 94.64% and 90% respectively. The maximum efficiency found at concentration of inhibitor as 600ppm.

The electrochemical measurement analyses were shown in Table 2. The results indicated that anodic and cathodic current decreasing with increasing inhibitor concentration because of adsorption of inhibition molecules in mild steel surface. The results from polarization curve βa and βc parameters were decreased since anodic and cathodic process decline. Initially the inhibitor molecules adsorbed on the MS surface make corrosion inhibition in this way of mechanism cathodic hydrogen reaction and blocking active sites on the mild steel surface. Schiff base -OCH₃ group contained inhibitor results E₉₀Ο displacement exceeds about 32 mV which confirmed that studied compound is mixed type inhibitor. The 1M HCl and 0.5M H₂SO₄ acidic solutions in the presence inhibitor the efficiency found to be 85.2% and 81.8% respectively. The maximum efficiency found at concentration of inhibitor as 600ppm.

| Medium     | Inhibitor (ppm) | -E₉₀Ο(mV/SCE) | I₉₀Ο | -βc | βa | η(%) |
|------------|-----------------|----------------|------|-----|----|------|
| Blank      | 450             | 1.17           | 257  | 110 | -  | -    |
| 50         | 432             | 0.383          | 251  | 111 | 70.61 | 0.71 |
| 100        | 448             | 0.318          | 249  | 118 | 83.75 | 0.84 |
| 1M HCl     | 200             | 0.283          | 397  | 156 | 87.64 | 0.88 |
|            | 400             | 0.209          | 235  | 105 | 88.19 | 0.88 |
|            | 600             | 0.171          | 176  | 71.2 | 94.64 | 0.95 |
| Blank      | 455             | 2.930          | 245  | 143.9 | --- | --- |
| 50         | 451             | 1.116          | 124  | 81.9 | 75.98 | 0.76 |
| 100        | 448             | 0.841          | 138  | 69.3 | 82.05 | 0.82 |
| 0.5 H₂SO₄  | 200             | 0.729          | 122  | 69.5 | 87.43 | 0.87 |
|            | 400             | 0.638          | 130  | 75.9 | 88.37 | 0.88 |
|            | 600             | 0.533          | 124  | 77.7 | 90.00 | 0.90 |
Impedance studies

Nyquist plots shown in Fig. 7 and provide the impedance parameter such as charger resistance ($R_{ct}$), double layer capacitance ($C_{dl}$) and Inhibition efficiency (%) were specified in Table 3. The gradual decreases of $C_{dl}$ with increasing inhibitor concentration of Schiff base. This was happened since adsorbed inhibitor molecules on surface of MS. These adsorption processes useful for protect MS roughness increases by acid 1M HCl and 0.5M H$_2$SO$_4$. The protective layer thickness prolonged those are confirmed by semicircles diameter increase with concentration of inhibitor. These impedance behaviors conclude that the frequency dispersion ascribed roughness and homogeneities of solid surface$^{16}$.

Influence of temperatures on inhibition:

The inhibition efficiency at various temperatures range 303-333K were found by using impedance studies shown in Fig. 8 and listed in Table 4. It depicted that efficiency decreased since inhibited molecules desorption takes place. These are confirmed by the electrochemical impedance studies which elaborated charge transfer resistance ($R_{ct}$) decreased with increasing temperature.

Adsorption Isotherm

Inhibitor adsorption surface of metal has been investigated by Langmuir’s adsorption isotherm shown in Fig. 9 (a) and (b) for 1M HCl and 0.5M H$_2$SO$_4$ acidic solutions respectively. Schiff base involving chemical reaction on metal surface and transferred atom coverage the surface of MS. Langmuir’s adsorption isotherm model has been used under following equation$^{17}$.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + \frac{C}{\theta}$$

Where, C-Concentration of inhibitor, $\theta$-Fractional surface coverage and $K_{ads}$-Adsorption equilibrium constant.

Table 3: Impedance parameters of MS in inhibitor NB4MA presence of acidic solutions

| Medium          | Concentration of the Schiff base (ppm) | $R_{ct}$ (Ohm cm$^2$) | n  | $C_{dl}$ (μF cm$^{-2}$) | η(%) |
|-----------------|----------------------------------------|------------------------|----|-------------------------|------|
| Blank           |                                        | 19.1                   | 0.912 | 173                      | -    |
| 50              |                                        | 60.7                   | 0.926 | 97                      | 68.5 |
| 100             |                                        | 72.3                   | 0.933 | 73                      | 73.6 |
| 1.0 M HCl       | 200                                    | 88.8                   | 0.927 | 48                      | 78.5 |
|                 | 400                                    | 110.4                  | 0.973 | 32                      | 82.7 |
|                 | 600                                    | 134.5                  | 0.971 | 25                      | 85.8 |
| Blank           |                                        | 12.5                   | 0.909 | 207                     | -    |
| 50              |                                        | 34.5                   | 0.917 | 112                     | 63.8 |
| 100             |                                        | 44.4                   | 0.955 | 87                      | 71.9 |
| 0.5 M H$_2$SO$_4$| 200                                    | 51.6                   | 0.961 | 55                      | 75.8 |
|                 | 400                                    | 61.6                   | 0.947 | 42                      | 79.7 |
|                 | 600                                    | 71.1                   | 0.958 | 31                      | 82.4 |
Table 4: Temperature effect of inhibitor NB4MA in mild steel

| Temperature (K) | Charge transfer resistance (Ohm cm²) |
|-----------------|-------------------------------------|
|                 | 1M HCl                               |
|                 | 0.5M H₂SO₄                           |
| 303             | 134.4                                |
| 308             | 96.60                                |
| 313             | 70.20                                |
| 318             | 51.50                                |
| 323             | 38.10                                |
| 300 K           | 71.10                                |
| 308 K           | 51.60                                |
| 313 K           | 37.90                                |
| 318 K           | 28.10                                |
| 323 K           | 21.10                                |

The linear regression plot of C/θ against C gives correlation co-efficient ($R^2$) and slope closer to 1 which confirmed that inhibitor and MS and solutions interface follow this type of adsorption isotherm. $K_{ads}$ value calculated by using intercept in straight line of isotherm graph these values further used to calculate energy of adsorption ($ΔG_{ads}$).

**Thermodynamic parameters**

Free energy ($ΔG^0_{ads}$)
interaction occurs charged molecules were attracted on metal surface. Meanwhile, $\Delta G^0_{ads}$ value shows more negative values than -40kJmol$^{-1}$ since charge transfer forms co-ordinate bond facilitates chemisorption takes place due to electron transfer from molecules to the metal surface.

| Sample | $E_a$(kJ/mol) | $-\Delta G^0_{ads}$(kJ/mol) |
|--------|--------------|-----------------------------|
| 1.0 M HCl blank | 69.13 | - |
| 0.5 M H$_2$SO$_4$ blank | 61.23 | - |
| 1.0 M HCl+600 ppm of inhibitor | 51.28 | -27.09 |
| 0.5 M H$_2$SO$_4$+600ppm of inhibitor | 49.45 | -26.95 |

The synthesized Schiff base $\Delta G^0_{ads}$ found value found -27.09 and -26.95 for 1.0M HCl and 0.5M H$_2$SO$_4$ correspondingly in the presence of 600 ppm concentration of inhibitor has been used. The $\Delta G^0_{ads}$ higher than -20kJmol$^{-1}$ and not exceeds -40kJmol$^{-1}$ which concludes physisorption obeyed. However, another one thermodynamic parameter activation energy ($E_a$) of blank solution is higher than presence of inhibitor confirms adhere chemisorption since electron transferred from inhibitor metal surface forms co-ordinate type of bond. These concludes Schiff base initially involving electrostatic attraction further formed co-ordinate type of bond hence synthesized Schiff base adsorption mechanism on mild steel surface might be equally physisorption and chemisorption observed.

**Quantum chemical studies**

The Schiff bases HOMO and LUMO geometry are shown in Fig. 10. Quantum chemical parameters were calculated by the means of DFT method and listed in Table 6. The Frontier molecular orbital (FMO) theory concludes reactant HOMO and LUMO involving in interaction causes reaction is possible because $E_{HOMO}$ and $E_{LUMO}$ have electron donor and acceptor capability respectively. The quantum chemical parameters including ionization potential and electron affinity were determined by HOMO and LUMO behavior.

The benzylidene Schiff bases has been synthesized and investigated corrosion behavior in 1M HCl reported by U. J. Naik et al., and suggested that electron donating ability $\Delta N$<3.6 attributed metal surface has been protected by the inhibitor. The
inhibition efficiency enhanced since aromatic ring has –OCH₃ and –OH groups present in the Schiff base.

Table 6: Quantum chemical parameters of NB4MA

| Quantum chemical parameters | Values  |
|----------------------------|---------|
| $E_{\text{HOMO}}$(eV)      | -8.583  |
| $E_{\text{LUMO}}$(eV)      | -0.752  |
| $\Delta E$(eV)             | 7.831   |
| Ionization potential (I)   | 8.583   |
| Electron affinity (A)      | 0.752   |
| Hardness (η)               | 3.916   |
| Softness (α)               | 0.1277  |
| Electro negativity(χ)      | 4.668   |
| Electrophilicity index (ω) | 2.782   |
| Fraction of electron transferred (ΔN) | 0.2978 |
| Dipole moment (µ)          | 1.553   |

In our synthesized schiff base NB4MA quantum chemical parameter electron transfer ability (ΔN) value was found 0.2978 which confirms surface electron donating ability of inhibitor increased. The molecules electronic charge density diffused completely especially electronic density present in azomethine nitrogen as well as benzene aromatic ring. For that reason, synthesized Schiff bases have enhanced electron density hence higher coverage capacity of mild steel formed enormous inhibition efficiency.

**SEM analysis**

Figure 11 (a) and (b) showed scanning electron microscopy (SEM) images of MS present inside 1M HCl and 0.5M H₂SO₄ correspondingly. These exposed that the surface of mild steel scratched or damaged in the presence of acidic solutions. Meanwhile, Fig. 11 (c) and (d) shows morphology of MS presence of HCl and H₂SO₄ of 600 ppm concentration of inhibitor NB4MA respectively. It revealed that mild steel dissolution efficiency reduced and smooth surface shown since adsorption of inhibitor forms protective film on the metal surface.

Fig. 10. HOMO and LUMO of NB4MA

Fig. 11. SEM of (a) MS in HCl (b) MS in H₂SO₄ (c) MS in HCl + inhibitor (600ppm) (d) MS in H₂SO₄ + inhibitor (600ppm)

**CONCLUSION**

N-Benzylidene-4-Methoxyaniline Schiff base has been synthesized and studied their inhibition performance of mild steel. Further inhibition capacity investigated in existence of acidic solutions 1M HCl and 0.5 M H₂SO₄ with a various range concentration of inhibitor NB4MA. Weight loss method confirmed that inhibition efficiency has been enhanced with concentration of the inhibitors. The polarization and impedance studies confirm that both anodic as well as cathodic type of mixed inhibitor and inhibition capacity decreased with enhancing temperature. Thermodynamic parameter reveals that possible for both physisorption and chemisorptions process since-$\Delta G^0_{\text{ads}}$ about 20kJmol⁻¹ and activation energy decreased after adding inhibitor respectively. Quantum chemical parameter studies attributed that electronic charge density dispersing in the molecule causes induced corrosion efficiency for protect mild steel. SEM images shows smooth surface appeared in the presence Schiff base inhibitor because of protective layer formed surface of mild steel.

**ACKNOWLEDGEMENT**

The authors are greatful to PG and Research Department of Chemistry, Erode Arts and Science College (Autonomous), Erode, Tamilnadu, India for the provision of research facilities and also the laboratory facility.
REFERENCES

1. E L Basiony, N.M.; Amr. Elgendy, Nady, H.; Migahed, M. A.; Zaki, E. G. RSC Adv., 2019, 9, 10473-10485.
2. Belghiti, M.E.; Bouazama, S.; Echihi, S.; Mahsoune, A.; Elmoukky, A.; Dafali, A. E.; Emran, K.M.; Hammouti, B.; Tabyoui, M. Arab. J. Chem., 2020, 13, 1499-1519.
3. Ece Altunbas Sahin.; Faith Tezcan.; Ramazan Solmaz.; Gulfeza Kardas. J. Adhes. Sci. Technol., 2019. DOI: 10.1080/01694243.2019.1662202.
4. Nor Zakiah Nor Hashim.; El Hassane Anouar.; Karimah Kassim.; Hamizah Mohd Zaki.; Abdulrahman I. Alharthi.; Zaidi Embong., J. Mol. Liq., 2020, 317, 114015.
5. Bedair, M. A.; Soliman, S. A.; Mostafa F. Bakr.; Gad, E. S.; Hassane Lgaz, Ill- Min. Chung, Mohamed Salama, Faleh Z. Algahtany., J. Mol. Liq., 2020, 317, 114015.
6. Abdelghani Madani.; Lakhdar Sibous.; Abdelkader Heilal.; Ilhem Kaabi.; Embarek Bentouhami., J. Mol. Struct., 2021, 1325, 130224.
7. Caio Machado Fernandes.; Lucas Guedes.; Leonardo X. Alvarez.; Adriana M. Barrios.; Hassane Lgaz.; Han-Seung Lee.; Eduardo A. Ponzio., J. Mol. Liq., 2022, 363, 119790.
8. Hulya Keles.; Mustafa Keles.; Koray Sayin., Corros. Sci., 2021, 184, 109376.
9. Lijun Wang.; Xiaoyan Yin.; Weiyun Wang.; Lei Ji.; Zhongfang Li. Int. J. Electrochem. Sci., 2014, 9, 6088-6102.
10. Mohanapriya, T.; Kumar, P. E. Int. J. Res. Eng. Appl. Manag., 2018, 4, 351-359.
11. Karima Abderrahim.; Sihem Abderrahmane.; Jean-Pierre Millet. Iran. J. Chem. Eng., 2016, 35, 89-98.
12. Reeja Johnson.; Joby Thomas Kakasserry.; Vinod Raphael Palayoor.; Ragi Kooliyat.; Vidhya Thomas Kannanaikkal. Orient. J. Chem., 2020, 36, 1179-1188.
13. Charles, A.; Sivaraj, K.; Thanikaikarasan, S. Mater. Today proceedings., 2020, 33, 3135-3138.
14. Shaimaa B. Al-Bghdadi.; Mahdi M. Hanoon.; Jafer F. Odah.; Lina M. Shaker.; Ahmed A. Al-Amiery., Proceedings., 2019, 41, 1-9.
15. Behpour, M.; Mohammadi, N.; Alin, E. J. Iron Steel Res. Int., 2014, 21, 121-124.
16. Dasami, P. M.; Parmeswari, K.; Chitra, S. Measurement., 2015, 69, 195-201.
17. Mohanapriya, T.; Kumar, P. E. Int. J. Innov. Res. Sci. Eng. Tech., 2016, 5, 18706-18722.
18. Hegazy, M.A.; Ahmed.; H. M.; El-Tabei.; A.S. Corros. Sci., 2011, 53, 671-678.
19. Naik, U. J.; Shah, N.K. Maghreb. J. Pure and Appl. Sci., 2016, 2, 1-16.
20. Kosari, A.; Moayed, M. H.; A. Davoodi, A.; Parvizi, R.; Momeni, M.; Eshghi, H.; Moradi, H. Corro. Sci., 2014, 78, 138-150.