



Synthesis and Evaluation of Anti-Corrosive Effect of new Thiourea based Schiff Base towards Steel Corrosion in Acidic Medium

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Abstract The Schiff base N,N'-bis[(3,4-dihydroxy-5-nitrophenyl) methylidene] thiourea (BDHNPMTU) was synthesized by the condensation of 3,4-dihydroxy-5-nitro-benzaldehyde with thiourea in acidic medium. The structure of BDHNPMTU was characterized by using elemental analysis, FT-IR and UV-Vis methods. The anti-corrosive effect of BDHNPMTU towards the corrosion of steel in 0.5M HCl was examined using mass loss measurement method. Result of study shows that BDHNPMTU is an effective inhibitor for steel corrosion in 0.5M HCl solution. The inhibition efficiency of BDHNPMTU increases with rising exposure time or immersion time. Inhibition efficiency of Schiff base increases with the increase the concentration of inhibitor and maximum Inhibition efficiency 96.5% at 48 hour immersion time shown at 5% (5×10^{-5} M) inhibitor concentration. Adsorption of the inhibitor on the steel surface followed Langmuir adsorption isotherm.

Keywords Corrosion, steel, Thiourea, Schiff base, Langmuir adsorption isotherm, Mass loss measurement

Introduction

Corrosion is a process in which material (metal & non-metal) surface degraded by its environment. In this process pure metal convert in impure form (like oxide, sulphide, halide etc.). So it is a serious problem for development of society it leads to significant loss to the economy, serious disasters and leads to pollution, so its prevention and control is good for the society. Iron and its alloy steel is widely used industrial metal in the world. Main ingredients of steel are Mn, Sn, Cr, Zn, C, Fe etc. Basically steel resistive towards its environment, but in strong acidic medium it surface get corroded. Hydrochloric acid is generally used for the removal of rust on the surface of steel/metals during industrial practices [1-3].

Corrosion of metals and its alloys is a serious issue for society and researchers. In present time different corrosion control techniques are used for prevention of corrosion of metals/alloys. The use of corrosion inhibitor is also a practical, safe, effective and ecofriendly method to control corrosion of metals/alloys.

Thiourea and its derivatives are having wide ranges of applications in medicinal, agriculture, analytical and metallurgy fields. Thiourea and its derivatives like Schiff bases are widely examined in last few decades as corrosion inhibitor for metals and alloys in acidic medium. Thiourea derivatives are potential class corrosion inhibitors for metals/alloys due to the presence of nitrogen and sulphur atoms in their structure. The presence of aromatic system also improves inhibition efficiency of inhibitors [4-14].

In this research article anticorrosive property of thiourea based Schiff base N,N'-bis[(3,4-dihydroxy-5-nitrophenyl)methylidene]thiourea (BDHNPMTU) against steel corrosion in 0.5M HCl studied.



2. Synthesis and characterization of Schiff base N,N'-bis[(3,4-dihydroxy-5-nitrophenyl) methylidene] thiourea (BDHNPMTU)

2.1. Synthesis of Schiff base BDHNPMTU

The Schiff base BDHNPMTU was synthesized and characterized on the basis of review of literature [14-25]. Analytical grade reagents were used in this synthesis. The Schiff base BDHNPMTU was synthesized by the condensation of 3,4-dihydroxy-5-nitro-benzaldehyde with thiourea in acidic medium. The content was refluxed on heating mantle about 4-5 hours at 70°C with water condenser. On cooling the dark brown coloured solid with M.P.110°C was separated out. The method of synthesis is summarized in Figure (1).

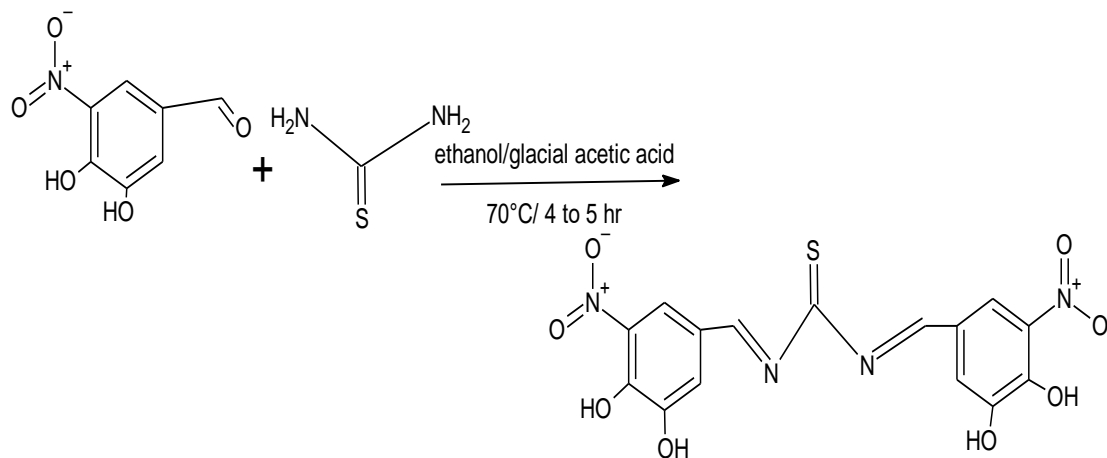


Figure 1: Scheme of synthesis of schiff base

2.2 Characterization of BDHNPMTU

The structure of compound was characterized by elemental analysis, IR and electronic studies. The elemental study shows the presence of C (44.34%), H (2.48%), N (13.79%), O (31.50%) and S (7.89%) in the compound. Absence of a $\nu(\text{C}=\text{O})$ band of aldehyde and presence of band of azomethine group $\nu(\text{C}=\text{N})$ occurred at $1690\text{-}1640\text{ cm}^{-1}$ in the IR spectra of BDHNPMTU indicating the synthesis of Schiff base. In IR spectra of BDHNPMTU different bands were also observed such as -O-H str. between $3500\text{-}3700\text{ cm}^{-1}$, broad band of N-H str. between $3100\text{-}3400\text{ cm}^{-1}$, -N-O str. of -NO_2 group at $1515\text{-}1560\text{ cm}^{-1}$, $1345\text{-}1385\text{ cm}^{-1}$ and C-S str. of $\text{C}=\text{S}$ group at $\sim 725, \sim 1100\text{ cm}^{-1}$.

In the electronic spectrum of BDHNPMTU $n \rightarrow \pi^*$ absorption peak of azomethine group were observed at 310.5, 320.5, 341.5, 354, 370 nm and $\pi^* \rightarrow \pi^*$ peak of benzene ring observed at 249.5nm.

3. Experimental

For the mass loss measurements rectangular steel specimens (with zinc coated) of size 3.0cm x 2.5cm x 0.045 cm. Before study all the specimen dried in acetone and stored in moisture free desiccators before their use in mass loss studies. Acid and inhibitor solutions were prepared in double distilled water. .01M inhibitor solution was used for mass loss study.

Each specimen was suspended by a V- shaped glass hook made by capillary glass tube and immersed in a glass beaker containing 50 ml of test solution at room temperature. After the exposure of sufficient time the test specimen was taken out, cleaned under running water and dried in oven, after drying specimens weighted. The variation in mass loss was followed at an interval for 4 hours to 48 hours in 0.5M HCl at 20°C as shown in the tables 1.

The percentage corrosion inhibition efficiency was calculated as:

$$\eta\% = 100 (\Delta M_a - \Delta M_i) / \Delta M_a$$

Where, ΔM_a = Mass loss of steel only in acid solution.

ΔM_i = Mass loss of steel in presence of inhibitor.



The degree of Surface coverage (θ) of metal specimen by inhibitor was calculated as:

$$\theta = (\Delta M_a - \Delta M_i) / \Delta M_a$$

The corrosion rates (CR) can be calculated by the following equation:

$$CR \text{ (mm / yr)} = (\text{Mass loss} \times 87.6) / \text{DAT}$$

Where, D = density of steel (7.84g/cm³)

A = surface area of steel specimen

T = time exposure

4. Result and Discussion

In this study corrosion parameter of steel corrosion in 0.5M HCl measured using mass loss method at constant temperature 20°C. Here we discuss mainly effect of two factors namely immersion time and inhibitor concentration on inhibition efficiency of inhibitor. On the basis of corrosion parameters shown in table 1 it is clear that the corrosion of steel in 0.5M HCl increases with Immersion time. The inhibition efficiency of BDHNPMTU increases with rising exposure time or immersion time. Corrosion rate values decrease as the concentration of inhibitor increases. Inhibition efficiency of Schiff base increases with the increase the concentration of inhibitor and maximum Inhibition efficiency (96.5% at 48 hour immersion time) shown at 5% (5X10⁻⁵M) inhibitor concentration. The surface coverage increases with concentration of inhibitor, it shows the adsorption of inhibitor on steel surface. The images of surface of steel in presence and absence of inhibitor also support inhibition of corrosion. The graph log ($\theta/1-\theta$) versus logC(mol/L) show linearity it means adsorption of inhibitor obey Langmuir adsorption isotherm.

Table 1: Concentration of inhibitor (COI %), mass loss ΔM (in mg), inhibition efficiency η (%), surface coverage and corrosion rate CR (in mm/year) for steel in presence of BDHNPMTU at different time interval

COI	4 hours				12 hours				24 hours				48 hours			
	ΔM	η	θ	CR	ΔM	η	θ	CR	ΔM	η	θ	CR	ΔM	η	θ	CR
blank	.06508	.12338	.18253	.23	2.1
1	.032	47.3	.473	.271	.056	53.3	.533	.158	.08	55.5	.555	.112	.095	58.7	.587	.067
2	.021	65	.65	.177	.04	66.6	.666	.112	.052	71.1	.711	.073	.058	74.7	.747	.041
3	.015	75	.75	.127	.026	78.3	.783	.073	.034	81.1	.811	.047	.034	85.6	.856	.024
5	.008	86.6	.866	.067	.011	90.4	.904	.031	.013	93.2	.932	.018	.008	96.5	.965	.005

5. Conclusion

The inhibition ability of synthesized thiourea based Schiff base BDHNPMTU as corrosion inhibition for steel in 0.5M HCl have been studied. Some conclusion made on basis of mass loss measurements are:

- BDHNPMTU act as excellent inhibitor for steel corrosion in 0.5M HCl.
- The inhibition efficiency of inhibitor increases with concentration of inhibitor.
- The inhibitor is effective over long time and it show maximum efficiency 96.5% at 48th hour immersion time
- Adsorption of inhibitor obey Langmuir adsorption isotherm.

6. Research Gap

Thiourea based Schiff base BDHNPMTU is nontoxic and soluble in aqueous media. It have nitrogen, sulphure atom and aromatic system in their structure. So, these properties would justify the use of Schiff base of thiourea as corrosion inhibitor. The synthesis of new thiourea derivative plays an important role in development of efficient inhibitor for metals/alloys corrosion in acidic medium in future.

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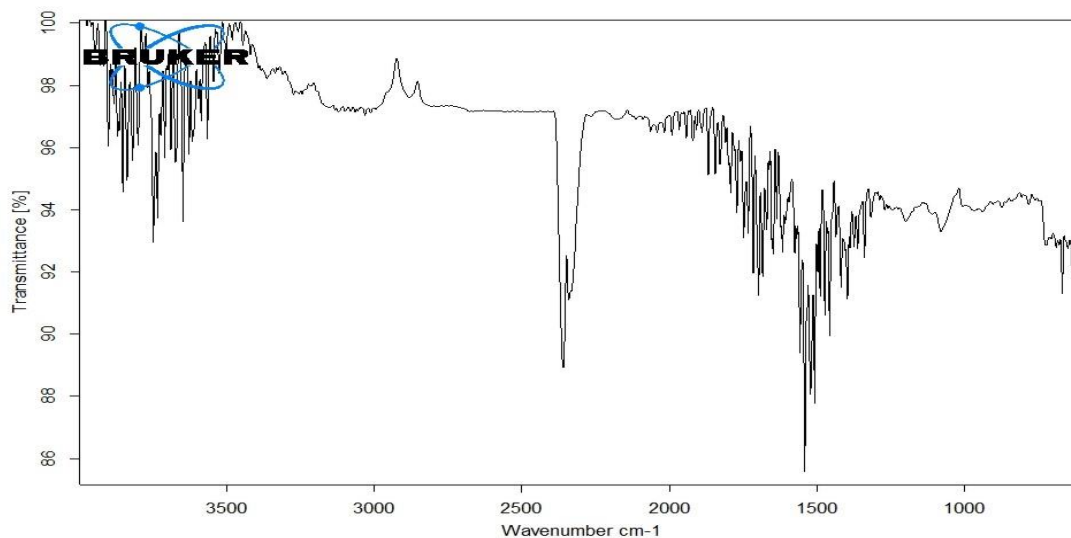


Figure 2: IR spectrum of BDHNPMTU

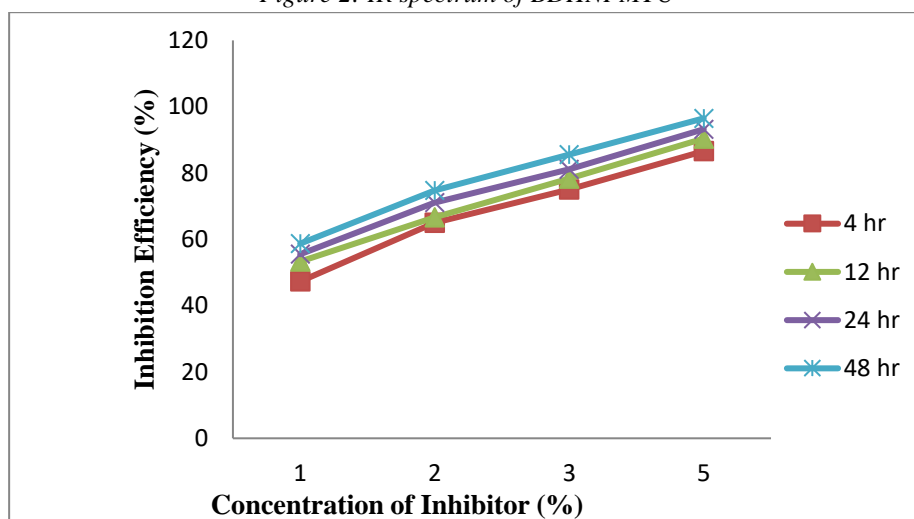


Figure 3: The graph inhibition efficiency v/s concentration of inhibitor (%) at different time interval for steel in 0.5 M HCl

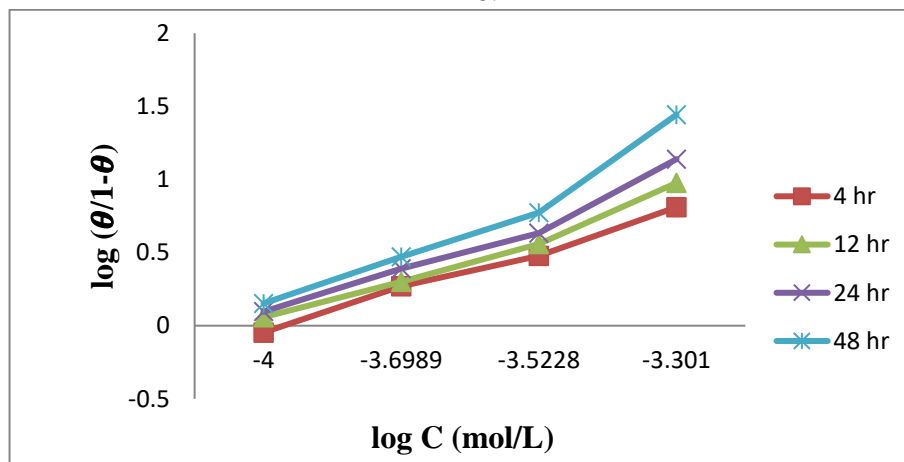


Figure 4: Langmuir adsorption isotherm plot for steel with Schiff base BDHNPMTU in 0.5M HCl



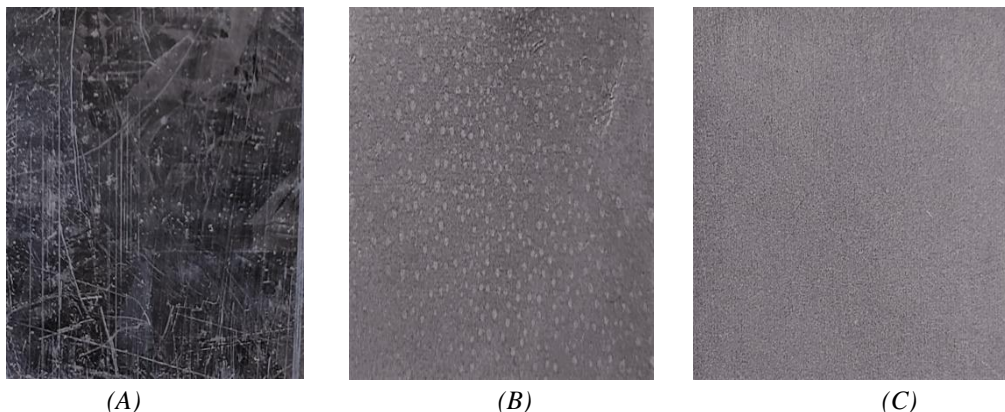


Figure 5: Steel surface (A) Fresh (B) In 0.5 M HCl (C) In presence of BDHNPMTU

References

- [1]. Uhlig H H and Revie R W, *Corrosion and Corrosion Control*, Wiley, New York, (1985).
- [2]. Ahmad I, Prasad R and Quraishi M A, *Corrosion Science*, 52(2010) 3033-3041.
- [3]. <https://www.tatasteel.com>
- [4]. Al-Amiery A, Kadhum A, Alobaidy A H, Mohamad A, Hoon P, “Novel Corrosion Inhibitor for Mild Steel in HCl”, *Materials*, 7(2014) 662– 672.
- [5]. Kumar S, Kumawat A and Swami V K, “A Study of Corrosion Inhibition Effect of Thiosemicarbazide based Schiff Base on Aluminium metal in Acidic Medium”, *Journal of Global Resources*, 08(01) (2021) 94-98.
- [6]. Harikumar S, Venkatachalam G, Narayan S and Venkatesh R, “The inhibitive action of Cyclohexyl thiourea on corrosion and hydrogen permeation through mild steel in acidic solution”, *International Journal of ChemTech Research*, 4(3) (2012) 1065-1071.
- [7]. Aldesoky A M, “Interaction of Thiourea Derivatives with a C-Steel Surface: Towards the Development of ‘Green’ Corrosion Inhibitors”, *International Journal of Scientific & Engineering Research*, 5(11) (2014) 330-341.
- [8]. Desai M N, Thanki G H and Gandhi M H, “Thiourea and its derivatives as corrosion inhibitors”, *Anti-Corrosion Methods and Materials*, 15(07) (1968) 12-16.
- [9]. Quraishi M A, Ansari F A and Jamal d, “Thiourea derivatives as corrosion inhibitors for mild steel in formic acid”, *Materials Chemistry and Physics*, (2003)
- [10]. Huong D Q, Duong T and Nam P C, “Effect of the Structure and Temperature on Corrosion Inhibition of Thiourea Derivatives in 1.0 M HCl Solution”, *ACS Omega*, 4(11) (2019) 14478–14489.
- [11]. Lavanya D K, Frank V P, Vijaya D P and Bangera S, “Inhibition Effect of Thiourea Derivatives for Mild Steel Corrosion in acidic Medium: Experimental and Theoretical Studies”, *J Bio Tribo Corros*, 7(2021) 47.
- [12]. Weder N, Alberto R and Koitz R, “Thiourea Derivatives as Potent Inhibitors of Aluminum Corrosion: Atomic-Level Insight into Adsorption and Inhibition Mechanisms” *J. Phys. Chem. C*, 120(03) (2016) 1770-1777.
- [13]. Agrawal R and Nambodhiri T K G, “The inhibition of sulphuric acid corrosion of 410 stainless steel by thioureas,” *Corrosion Science*, 30(01) (1990) 37–52.
- [14]. Kumar S and Swami V K, “A Comparative Study of Inhibition Effects of Some New Schiff bases on Copper Corrosion in Acidic Medium”, *Journal of Advanced Scientific Research*, 13(2) (2022) 176-182.



- [15]. Hashim S N M, Juliana J and Karimah K, "Synthesis and Corrosion Inhibition Studies of 1-(4-chlorobenzoyl)Thiourea Derivatives on Mild Steel in 1.0 M HCl", *Advances Science Letters*, 23(05) (2017) 4523-4527.
- [16]. Kumar S and Swami V K, "Corrosion Inhibition Effect of Newly Schiff Base on Iron Metal in 1M Hydrochloric Acid", *Remarking an Analisation*, 4(1) (2019) 259-263.
- [17]. Naz S, Zahoor M, Umar M N, Alghamdi S, Sahibzada M U K and Ulbari W, "Synthesis, characterization and pharmacological evaluation of thiourea derivatives", *Open Chemistry*, 18(01) (2020) 764-777.
- [18]. Oliveira C G M, Faria V W, Andrade G F et al., "Synthesis of Thiourea Derivatives and its Revaluation as Corrosion Inhibitor for Carbon Steel", *Tandpole*, (2015) 1366-1377.
- [19]. Kumar S and Swami V K, "Corrosion Inhibition Effect of Newly Schiff Base on Copper Metal in 1M Hydrochloric Acid", *Journal of Advanced Scientific Research*, 11(4) (2020) 337-340.
- [20]. Kumar S, Chahar Y and Swami V K, "A Study of Newly Schiff Base as Corrosion Inhibitor for Metal Corrosion in Acidic Medium", *International Journal of Trend in Scientific Research and Development (IJTSRD)*, 5(5) (2021) 1945-1950.
- [21]. Sukla S N, Gaur P, Vaidya P et al., "Synthesis, Computational and Spectroscopic studies of some Thiourea Schiff base metal complexes and its applications as Corrosion Inhibition, Catalase like activity and Antimicrobial screening", *International Journal of Basic and Applied Chemical Sciences*, 8(2) (2018) 1-19.
- [22]. Dohare P Quraish M A and Obot I B, "A Combined electrochemical and theoretical study of pyridine-based Schiff bases as novel corrosion inhibitors for mild steel in hydrochloric acid", *J. Chem. Sci.*, 8(130) (2018) 1-19.
- [23]. Balaji M, Chandrashekhar N, Sharmila G and Manivannan R, "Synthesis and evaluation of Anti-corrosive behavior of some Schiff base derivative", *IMPACT: IJRET*, 4(6) (2016) 51-64.
- [24]. Yadav M, Kumar S, Bahadur I and Ramjugernath D, Corrosion Inhibitive Effect of Synthesized Thiourea Derivative on Mild Steel in a 15% HCl Solution", *Int. J. Electrochem. Sci.*, 9(2014) 6529-6550.
- [25]. Beilstein V S, "Mechanochemical synthesis of thioureas, ureas and guanidines", *J. Org. Chem.*, 13(2017) 1828-1849.

