

Corrosion Inhibition Effect of Newly Schiff Base on Iron Metal in 1m Hydrochloric Acid



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Abstract

The Schiff base N,N'-bis[(3,4-dihydroxy-5-nitrophenyl)methylidene]thiourea (BDHNPMTU) synthesized by condensation of 3,4-dihydroxy-5-nitro-benzaldehyde and thiourea. The structure of Schiff base was fully characterized by elemental analysis, FT-IR and UV-Vis methods. The inhibition effect of BDHNPMTU towards the corrosion on iron in 1M HCl was investigated using weight loss measurement technique and scanning electron microscope (SEM). Results showed that BDHNPMTU is an effective inhibitor for iron corrosion in 1.0 M HCl solution. The inhibition efficiency also increased with concentration of inhibitor increased. Maximum inhibition efficiency is shown at highest concentration of inhibitor 5% ($5 \times 10^{-5} \text{M}$). Adsorption of the inhibitor on the iron surface followed Langmuir adsorption isotherm. Morphological study of metal surface also supports the corrosion inhibition of iron by BDHNPMTU.

Keywords: BDHNPMTU, Corrosion, Inhibition Efficiency, Iron, Weight Loss Measurement.

Introduction

Corrosion is a very common phenomenon in industries and it has wide amount of interest because of its hazardous nature on metals. Corrosion has a huge economic and environmental impact on all facets of national infrastructure. It is a constant and continuous problem, often difficult to eliminate completely [1-3]. Evaluation of corrosion inhibitors for mild steel/iron in acidic media is important for some industrial facilities. Acid solutions are generally used for the removal of rust and scale in industrial processes. Hydrochloric acid is widely used in the pickling, and cleaning of steel/iron [4]. The use of inhibitor is one of the most practical methods for protection against corrosion to protect metal dissolution and acid consumption [5]. Organic compounds containing a heteroatom (N, O and S) in their structure act as good corrosion inhibitors. The corrosion inhibitor efficiency of organic inhibitor are depends on the chemical structure and physiochemical properties of the compound like functional groups, electron density at the donor atom, *p*-orbital character, and the electronic structure of the molecule [6-10]. Recently the use of synthetic inhibitors has created environmental problems due to its toxicity properties. Thus it is important and necessary to develop low cost and environmentally safe corrosion inhibitors [11-15].

Schiff bases form an important class of the most widely used organic compounds and has a wide variety of applications in many fields including analytical, biological and inorganic chemistry [16]. In recent years, the efficiency of Schiff bases as organic corrosion inhibitors has been studied in a wide range. Thiourea and its derivatives have been studied for more than four decades because they inhibit effectively the corrosion of steels/iron in acid media [17-32]. The Schiff base of thiourea (BDHNPMTU) is nontoxic, soluble in aqueous media, relatively cheap and easy to produce with high purity. These properties would justify the use of Schiff base of thiourea as corrosion inhibitor.

The aim of the present paper is to study the anticorrosive properties of Schiff base (BDHNPMTU) on iron corrosion in a strong acidic media.

Synthesis and Characterization of BDHNPMTU**Synthesis of BDHNPMTU**

All the reagents used in this study were of analytical grade. 3,4-dihydroxy-5-nitro-benzaldehyde, thiourea and glacial acetic acid were obtained from (SLR, India). The BDHNPMTU was synthesized and characterized on the basis of past various research studies done so far [33-40]

The N,N'-bis[(3,4-dihydroxy-5-nitrophenyl)methylidene]thiourea (BDHNPMTU) was

synthesized by the condensation of 3,4-dihydroxy-5-nitro-benzaldehyde and thiourea in equal molar ratio in ethanol (20ml) in presence of glacial acetic acid(2ml). The content was refluxed for about 4-5 hours at 70°C with water condenser. On cooling the dark brown coloured solid (M.P.110°C) separated out. The same was filtered, washed with 50% ethanol, recrystallised in ethanol. The method of synthesis is summarized in Figure (1).

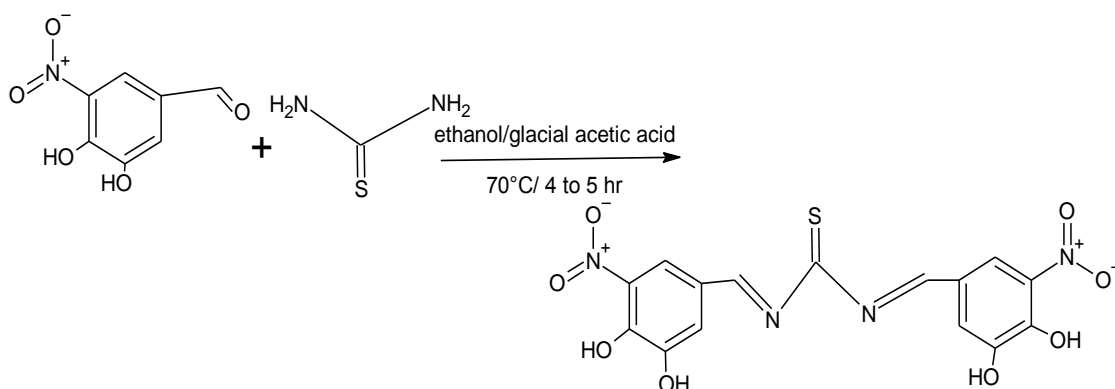


Figure 1: Reaction scheme

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 $\nu(\text{C}=\text{N})$ band occurred at $1690\text{-}1640\text{ cm}^{-1}$ in the IR spectra of BDHNPMTU indicating the condensation between aldehyde group of 3,4-dihydroxy-5-nitro-benzaldehyde and amino group of thiourea. 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 $n\text{-}\pi^*$ absorption peak of azomethine group were observed at 310.5, 320.5, 341.5, 354, 370 nm and $\pi^*\text{-}\pi^*$ peak of benzene ring observed at 249.5nm.

Experimental**Weight Loss Measurements**

For the mass loss study rectangular iron specimens of size 3.0cm x 2.5cm x 0.1 cm was employed with a small hole of about 0.02 cm. diameter near the upper edge were employed. The specimens were mechanically polished with different grades of emery paper; they were degreased in absolute alcohol, dried in acetone and stored in moisture free desiccators before their use in adsorption studies. All the chemicals employed were of analytical grade and the corresponding solutions were prepared in double distilled water. .01M inhibitor solution was used for corrosion 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 72 hours in 1M HCl as shown in the **table 1**.

The percentage corrosion inhibition efficiency was calculated as:

$$\% = 100 (\Delta M_U - \Delta M_i) / \Delta M_U$$

Where, ΔM_U = Mass loss of metal in uninhibited solution.

ΔM_i = Mass loss of metal in inhibited solution.

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

$$\Theta = (\Delta M_U - \Delta M_i) / \Delta M_U$$

The corrosion rates can be calculated by the following equation:

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

Where, D = density of copper

A = surface area of metal specimen

T = time exposure

Surface Morphological Study

The surface morphology of the formed layers on the iron surface after its immersion in the solutions of 0.5 M HCl in the absence and in the presence of Schiff's base BDHNPMTU (at various concentrations) were carried out by scanning electron microscope (SEM) [Fig.4].

Result and Discussion

The inhibition of corrosion is a complex phenomenon and the efficiency of inhibitor depends on various factors. In this paper we discuss effect of two factors namely immersion time and inhibitor concentration. Immersion time can play a decisive role in the prevention of corrosion ability. BDHNPMTU have shown a decreasing in its inhibition performance by rising exposure time or immersion time. Corrosion rate values decrease as the concentration of inhibitor

increases. Consequently, inhibition efficiency values increase with the increase the concentration of inhibitor and maximum Inhibition efficiency shown at 5% ($5 \times 10^{-5}M$) inhibitor concentration. This is due to

the adsorption of inhibitor on the copper surface. Adsorption of inhibitor obey Langmuir isotherm. Morphological study of iron surface also supports the inhibitory effect of BDHNPMTU.

Table 1: Concentration of inhibitor (COI), mass loss, inhibition efficiency, surface coverage and corrosion rate for iron metal in presence of BDHNPMTU at different time interval

C O I(%)	4 hours				24 hours				48 hours				72 hours			
	ΔM (mg)	η (%)	Θ	CR (mm/y r)	ΔM (mg)	η (%)	Θ	CR (mm/y r)	ΔM (mg)	η (%)	Θ	CR (mm/y r)	ΔM (mg)	η (%)	Θ	CR (mm/yr)
blank	1.9	7.2	4.7	2.9	5.9	1.8	9.2	1.8
1	.98	49.5	.495	4.6	1.7	62.9	.62	1.1	2.9	50.8	.50	.89	4.1	55.4	.55	.84
2	.45	76.8	.768	1.7	1.3	71.1	.71	.85	1.7	71.2	.71	.52	3.5	61.9	.61	.72
3	.18	90.7	.907	.66	.65	86.4	.86	.40	1.2	79.6	.79	.37	2.2	76.0	.76	.45
5	.13	93.3	.933	.48	.52	89.1	.89	.32	.80	86.4	.86	.24	1.3	85.8	.85	.26

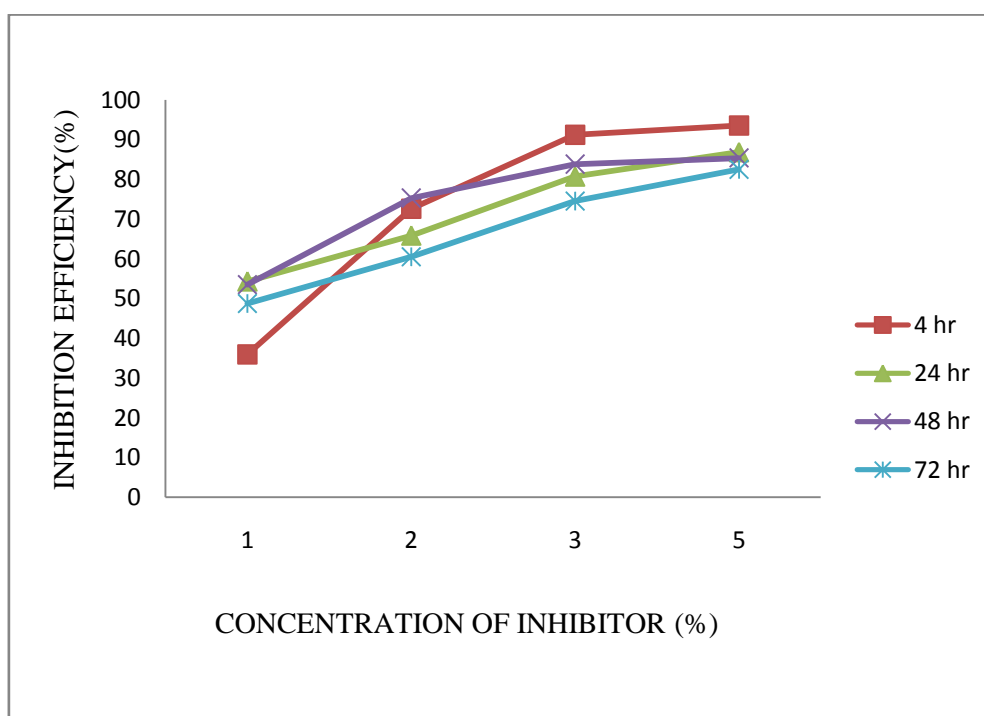


Figure 2: The graph inhibition efficiency v/s concentration of inhibitor (%) at different time interval for iron in 1 M HCl

Conclusion

The efficiency of synthesized Schiff base BDHNPMTU as corrosion inhibition for iron in acidic media have been studied. Results obtained from weight loss technique indicate that Schiff base act as potential inhibitor for iron corrosion in acidic media. Morphological study also support that BDHNPMTU is an effective corrosion inhibitor towards iron metal in

acidic condition. The graph between inhibition efficiency and concentration shows that the inhibition efficiency increases with concentration of inhibitor.

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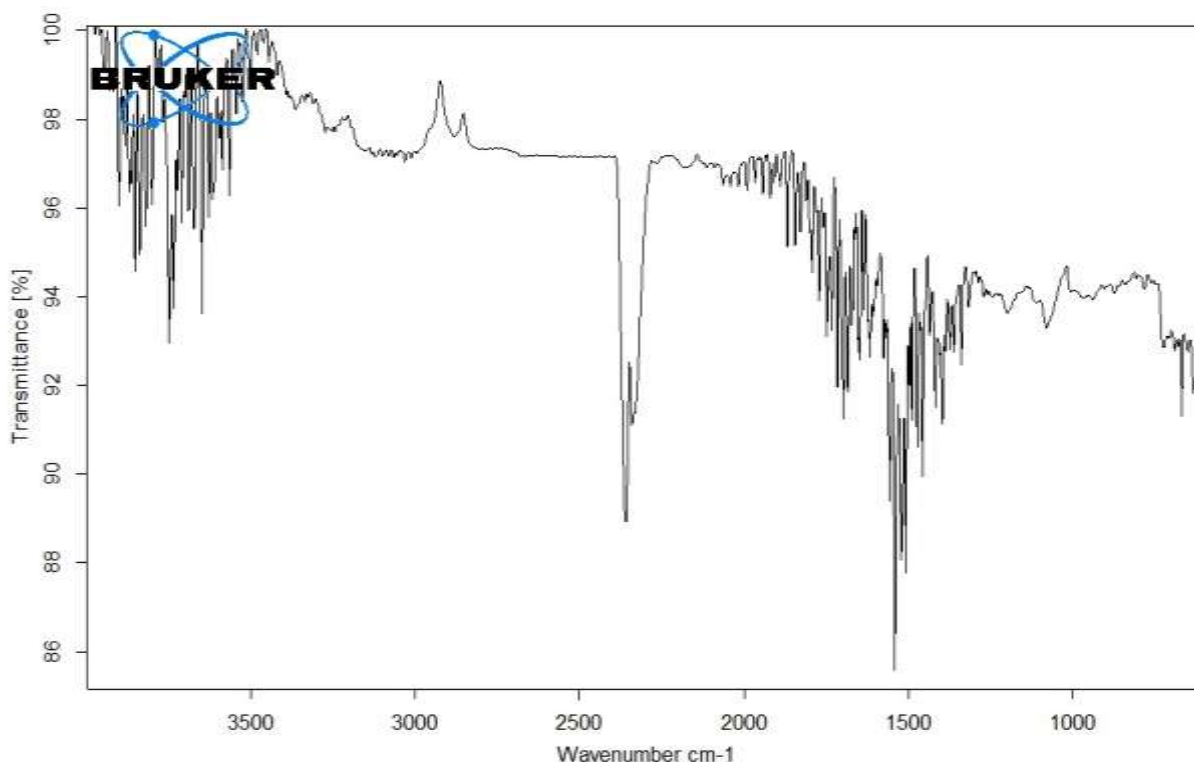
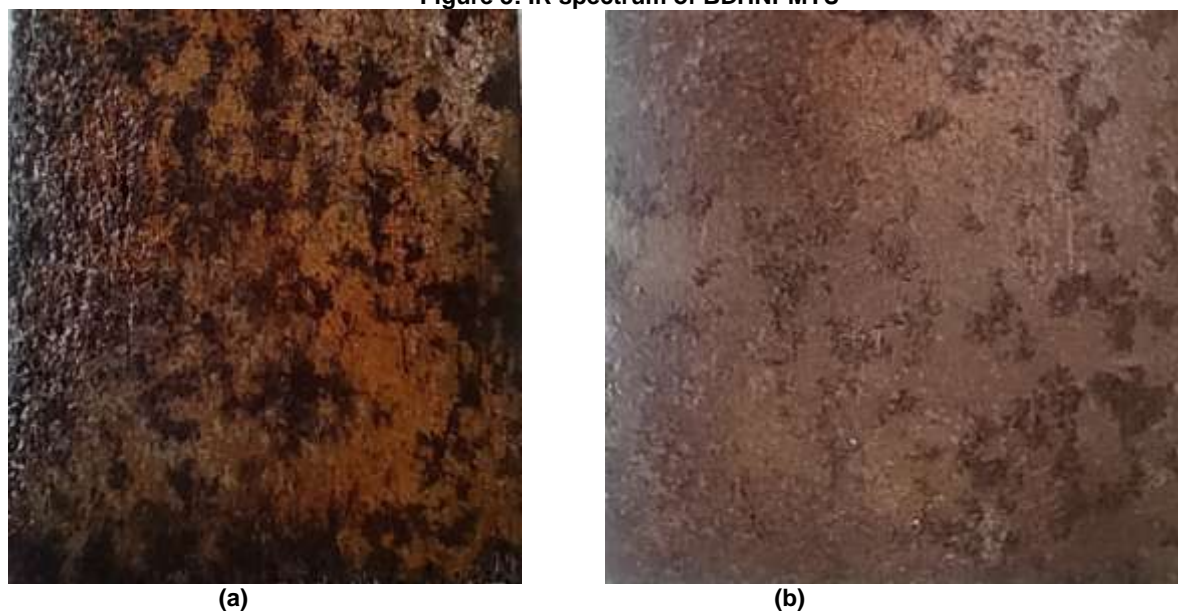


Figure 3: IR spectrum of BDHPMTU



(a) immersion of iron in 0.5 m HCl without inhibitor
(b) immersion of iron in 0.5 HCl with 5% inhibitor(BDHPMTU)

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