



CORROSION INHIBITION EFFECT OF NEWLY SCHIFF BASE ON COPPER METAL IN 1M HYDROCHLORIC ACID

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ABSTRACT

The Schiff base N,N'-bis[(3,4-dihydroxy-5-nitrophenyl) methylidene] thiourea (BDHNPMTU) was 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 copper in 1M HCl was investigated using weight loss measurement technique. Results showed that BDHNPMTU is an effective inhibitor for copper corrosion in 1.0 M HCl solution. It was found that when the concentration of the inhibitors was increased the inhibition efficiency was also increased. Adsorption of the inhibitor on the copper surface followed Langmuir adsorption isotherm. In 4 hr time duration Maximum inhibition efficiency (99%) is shown at highest concentration of inhibitor ($5 \times 10^{-5} \text{M}$).

Keywords: BDHNPMTU, Corrosion, Inhibition efficiency, Copper, Weight loss measurement.

1. INTRODUCTION

Copper is soft, malleable and ductile metal with very high thermal and electric conductivity [1, 2]. Copper is resistant toward the influence of atmosphere and many chemicals, however, it is known that in aggressive media it is susceptible to corrosion. Corrosion is a very common phenomenon in industries and it has wide amount of interest because of its hazardous nature on metals [3]. Due to the excellent mechanical properties and low cost, copper is extensively used as a constructional material in many industries. However, when exposed to the corrosive industrial environment, it is easily corroded. Normally, acid solutions such as hydrochloric acid are widely used such as in acid pickling, industrial cleaning, oil well cleaning, etc. The use of inhibitor is one of the most practical methods for protection against corrosion to protect metal dissolution and acid consumption [4]. Organic compounds containing a heteroatom (O, N and S) in their structure act as good corrosion inhibitors. They form a coordination bond with vacant d orbital of metal and form a protective layer on the surface of metal. The effectiveness of these organic molecules is based on their ability to form a protective layer by several mechanisms (*i.e.* adsorption, polymerization) [5-16].

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 [17, 18].

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 [19]. 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 copper in acid media. We have found that protective efficiency of the Schiff bases on copper corrosion strongly depends on the size and electronic effect of the substituents in molecule [20-31].

The Schiff base of thiourea (BDHNPMTU) is nontoxic, soluble in aqueous media, relatively cheap and easy to produce at high purity. These properties would justify the use of Schiff base of thiourea as corrosion inhibitor.

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

2. MATERIAL AND METHODS

2.1. 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 of obtained from (SLR,

India). The BDHNPMTU was synthesized and characterized on the basis of past various research studies done so far [32-37].

The N,N'-bis [(3,4-dihydroxy-5-nitrophenyl) methylene] thiourea (BDHNPMTU) was synthesized from 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 contents the dark brown coloured solid (M.P.110°C) separated out. The same was filtered, washed with 50% ethanol, recrystallized in ethanol. The method of synthesis is summarized in Fig. 1.

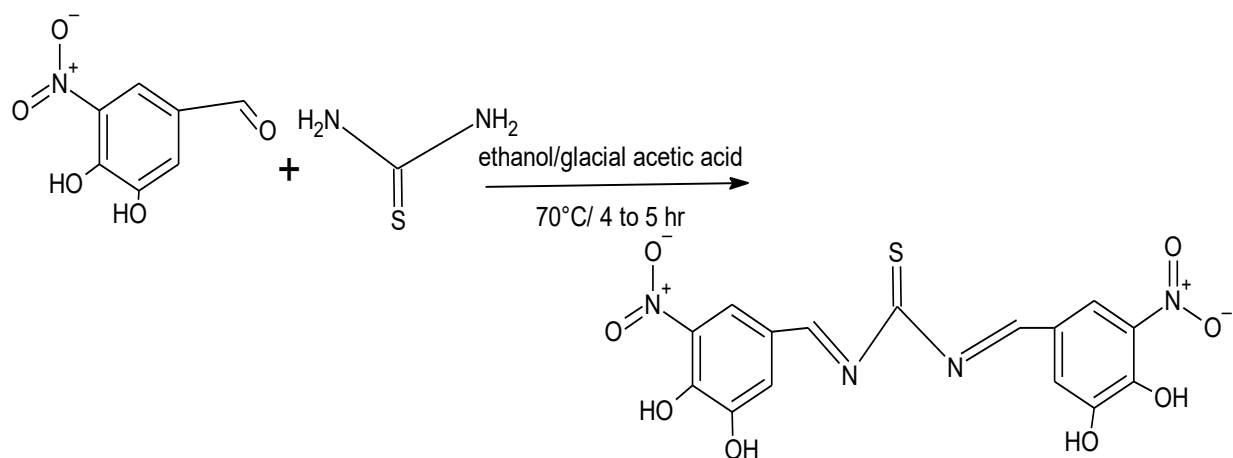


Fig. 1: Reaction scheme

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 $\nu(\text{C}=\text{N})$ band occurred at 1690-1640 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 the electronic spectrum of BDHNPMTU $n-\pi^*$ absorption peak of azomethine group were observed at 310.5, 320.5, 341.5, 354, 370 nm and $\pi-\pi^*$ peak of benzene ring observed at 249.5nm.

2.3. Experimental

For the mass loss study, rectangular copper specimen of size 3.0cm x 2.0cm x 0.1 cm was employed with a small hole of about 0.02 cm. diameter near the upper edge were employed. All the chemicals employed were of analytical grade and the corresponding solutions were prepared in double distilled water. 0.01M 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 Tables 1.

The percentage corrosion inhibition efficiency was calculated as

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

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:

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

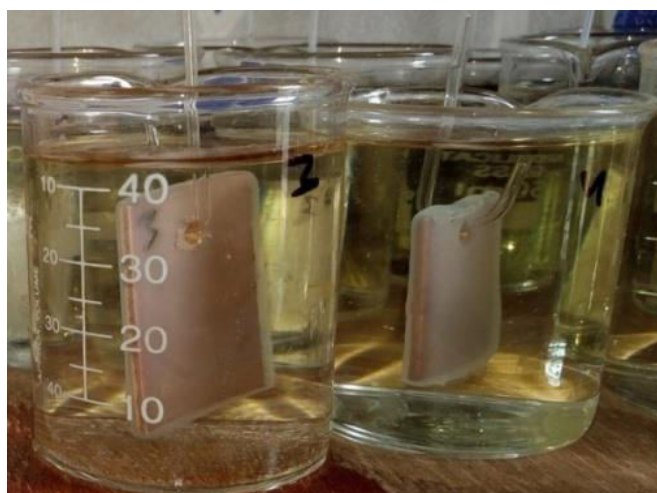
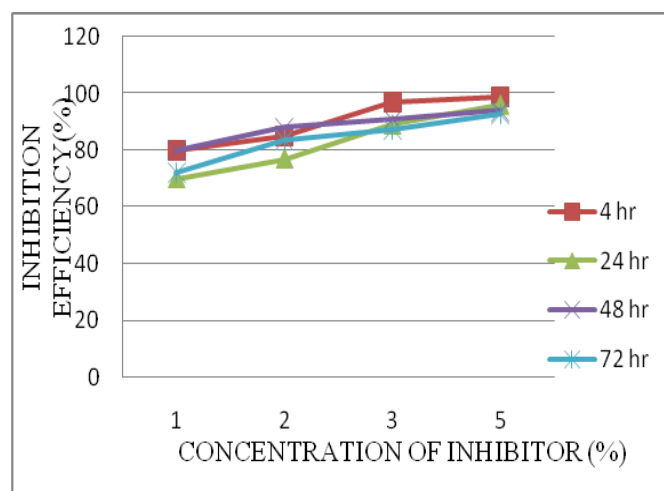
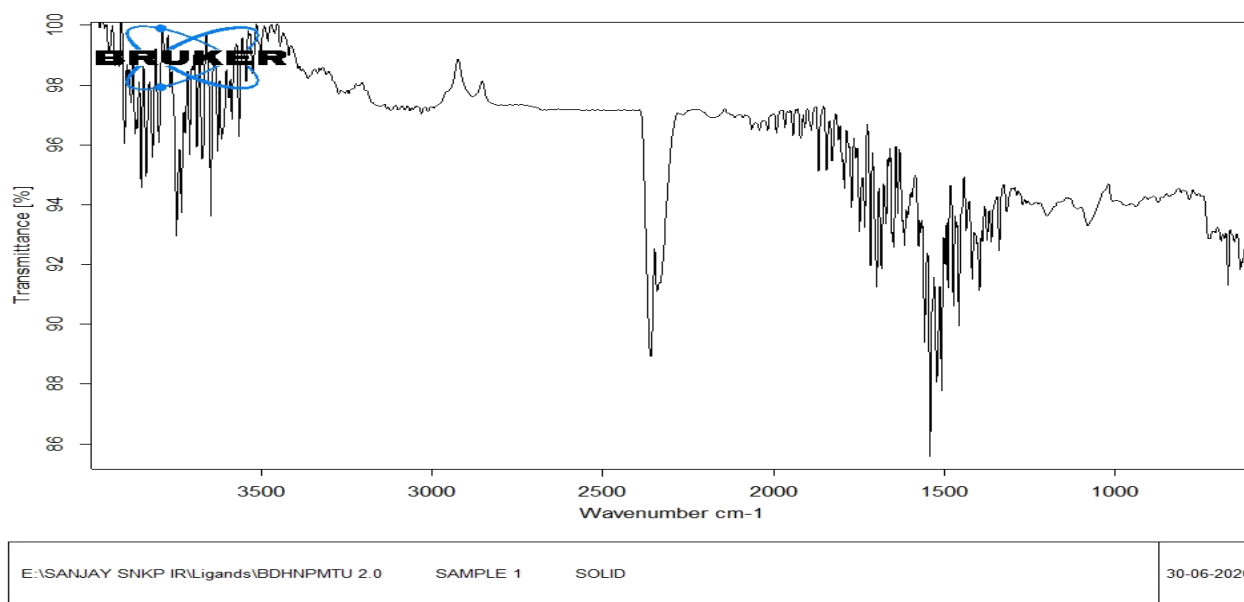
Where, D - density of copper, A - surface area of metal specimen, T - time exposure

3. RESULTS 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.

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

COI (%)	4 hours				24 hours				48 hours				72 hours			
	ΔM (mg)	η (%)	Θ	CR (mm/yr)	ΔM (mg)	η (%)	Θ	CR (mm/yr)	ΔM (mg)	η (%)	Θ	CR (mm/yr)	ΔM (mg)	η (%)	Θ	CR (mm/yr)
blank	0.2	0.81	0.27	0.18	2.9	0.98	2.2	0.68
1	0.04	80	0.80	0.16	0.08	70	0.7	0.05	0.56	80	0.8	0.19	0.62	72	0.72	0.14
2	0.03	85	0.85	0.12	0.06	77	0.77	0.04	0.36	88	0.88	0.12	0.37	83.6	0.83	0.08
3	0.005	97	0.97	0.02	0.03	89	0.89	0.02	0.24	91	0.91	0.81	0.28	87.2	0.87	0.06
5	0.002	99	0.99	0.008	0.01	96	0.96	0.006	0.17	94	0.94	0.05	0.16	92.7	0.92	0.03

**Fig. 2: The presence of protecting layer of BDHNPM TU on copper surface in 1M HCl****Fig. 3: The graph inhibition efficiency v/s concentration of inhibitor (%) at different time interval for copper in 1 M HCl****Fig. 4: IR spectrum of BDHNPM TU**

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 99 % shown at 5% (5×10^{-4} M) inhibitor concentration (4 hr). This is due to the adsorption of inhibitor on the copper surface (Fig. 2). Adsorption of inhibitor obey Langmuir isotherm.

4. CONCLUSION

The efficiency of synthesized Schiff base BDHNPMTU as corrosion inhibition for copper in acidic media has been studied. Results obtained from weight loss technique indicate that Schiff base act as efficient inhibitor for copper corrosion in acidic media. The graph between inhibition efficiency and concentration shows that the inhibition efficiency increases with concentration of inhibitor.

5. REFERENCES

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