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Navin Maharia Sanjay Kumar http://<u>www.sasjournals.com</u> http://<u>www.jbcr.co.in</u> jbiolchemres@gmail.com

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Corrosion Inhibition Effect of Pyridine Based Schiff Base on Copper Metal in Acidic Medium

Navin Maharia, Sanjay Kumar and V. K. Swami

Research Laboratory, Department of Chemistry, Govt. Lohia (PG) College, Churu, India

ABSTRACT

The Schiff base (E)-N-(5-bromopyridin-2-yl)-1-(4-ethylphenyl) methanimine (BPEPM) synthesized by condensation of 4-ethyl benzaldehyde and 2-amino-5-bromopyridine. The structure of Schiff base was fully characterized by elemental analysis, IR and NMR spectroscopic methods. The inhibition effect of BPEPM towards the corrosion of copper in 0.5M HCl was investigated using weight loss measurement technique. Results of study show that BPEPM is an effective inhibitor for copper corrosion in 0.5M HCl solution. The results of study show that inhibition efficiency of inhibitor increases with increasing concentration of inhibitor. Adsorption of the inhibitor forms a protecting layer on copper surface and retards the corrosion reaction. The inhibition efficiency of inhibitor increases with time duration. In 72 hour time duration Maximum inhibitior (5X10⁻⁵M).

Keywords: BPEPM, Corrosion, Inhibition efficiency, Copper and Weight loss measurement.

INTRODUCTION

Metals like Fe, Al, Cu etc. are main constituent of earth crust. They play an important role in human life and civilization. Metals and its alloys widely used in infrastructure development and electronic devices due to good mechanical strength and high conductance properties. Copper is widely used in chemical and microelectronic industries due to excellent electrical and thermal conductivity, good mechanical workability, relatively Nobel properties and good availability. Generally copper is resistant towards corrosion in mild conditions but in aggressive medium it get easily corroded. Corrosion is an undesirable phenomenon which destroys the luster and beauty of metals. Corrosion introduces in almost every part of our lives.

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It causes huge losses to buildings, automobiles, industries and their services [Mecafferty, 2010, Banerjee, 1985, Bardal, 2004, Meija et al., 2016, Meija et al., 2016, Moret et al., 2013, Uhlig and Revie, 1985].

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 [Gogoi and Barhai, 2011]. The use of corrosion inhibitor is a widely applied method for controlling corrosion. The corrosion inhibitors retard both anodic and cathodic reaction during corrosion process. Effectiveness of corrosion inhibitors depends on presence of hetero atoms (N, S, O etc.) and aromatic characters in their structure. Most of corrosion inhibitors are forming monolayer on the surface of metals in corrosive medium [Fareles et al., 2015, Joseph et al., 2011, Elmsellem et al., 2008, Kuznetsov et al., 2008, Curkovic et al., 2010, Khaled et al., 2011]. 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 [Swami and Kumar et al., 2019, Kumar and Swami, 2019].

Schiff bases form an important class of the most widely used organic compounds. Schiff bases widely tested as corrosion inhibitor for metals in acidic medium by many researchers. In recent years, Thiourea, pyridine, thiazole, phenol, thiasemicarbazide and its derivatives have been studied for more than four decades because they inhibit effectively the corrosion of copper in acid media [Hossain et al., 2018, Dave and Chopda, 2018, Behpour et al., 2012, Zhao and Cui, 2011, Al-Amiery et al., 2013]. The Schiff base of pyridine (BPEPM) 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 2-amino-5-bromopyridine as corrosion inhibitor.

The aim of the present study is to examine the anticorrosive properties of Schiff base of 2amino-5-bromopyridine (BPEPM) on copper corrosion in 0.5M HCl media.

MATERIAL AND METHODS

Synthesis of (E)-N-(5-bromopyridin-2-yl)-1-(4-ethylphenyl)methanimine (BPEPM)

All the reagents used in this study were of analytical grade. The BPEPM was synthesized and characterized on the basis of past various research studies done so far [Kuruvilla et al., 2016, Rizwana et al., 2012, Meena et al., 2018, Abirami et al., 2014, Al-Obaidi, 2012, Xavier, 2014]. The Schiff base (*E*)-*N*-(5-bromopyridin-2-yl)-1-(4-ethylphenyl)methanimine (BPEPM) synthesized by condensation of 4-ethyl benzaldehyde and 2-amino-5-bromopyridine. During synthesis process 2-amino-5-bromopyridine (0.1mole) and 4-ethyl benzaldehyde (0.1mole) dissolved in minimum quantity of ethanol has been taken in round bottom flask. The mixture has been refluxed over heating mantle for 7 to 8 hours, it was then cooled and resulting bright yellow colored crystals of BPEPM (M.P. 80°C) separated out. The crystals obtained have been then washed several times with ethanol, air-dried and recrystallized from ethanol. The method of synthesis is summarized in Figure (1).



Figure 1. Reaction Scheme.

Characterization of BPEPM

The structure of compound was characterized by elemental analysis, IR and NMR studies. The elemental study shows the presence of C (59.71%), H (4.20%), N (9.1%) and Br (26.40%) in the compound. Absence of a ν (C=O) band of aldehyde and presence of ν (C=N) band occurred at 1599.2 cm⁻¹ in the IR spectra (fig. 4) of BPEPM indicating the condensation between aldehyde group of 4-ethyl benzaldehyde and amino group of 2-amino-5-bromopyridine. In the NMR spectrum of BPEPM (fig. 5) various signals like -CH₃,-CH₂,-CH=N, Ar-H were observed at 1.2772, 2.7363, 7.3312, and 8.5232 δ (*ppm*).

Experimental

For the mass loss study rectangular copper specimens of size 3.0cm x 2.0cm x 0.1 cm was used. The corresponding solutions during study 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 0.5M HCl as shown in the tables 1.

The percentage corrosion inhibition efficiency was calculated as

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

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:

Corrosion rate (mm/yr) = (Mass loss x 87.6)/ DAT

Where, D = density of copper

A = surface area of metal specimen

T = time exposure

RESULT AND DISCUSSION

In this paper we discuss effect of two factors namely immersion time and inhibitor concentration. Immersion time can play an important role in the prevention of corrosion ability.

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According to the results of mass loss measurement it is clear that the corrosion rate decreases with increasing concentration of inhibitor (BPEPM) [fig.2]. The inhibition efficiency increases according increasing immersion time exposure [table 1]. Maximum Inhibition efficiency shows by inhibitor 98 % at 5% (5 X 10^{-4} M) concentration (72 hour immersion time). In corrosion process inhibitor form a protecting layer by adsorption on metal surface. This layer inhibits the further corrosion of metal surface. The surface coverage increases with increasing concentration of inhibitor. The plot between log (θ /1- θ) versus log C (mol/L) show linearity it means adsorption of inhibitor on copper surface obey Langmuir adsorption isotherm pattern [fig.3].

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

С	4 hours				24 hours				48 hours				72 hours			
0	ΔM	η	θ	CR	ΔM	η	θ	CR	ΔM	η	θ	CR	ΔM	η	θ	CR
I (%)	(mg)	(%)		(m	(mg)	(%)		(m	(m	(%)		(m	(m	(%)		(mm/
				m/y				m/y	g)			m/y	g)			yr)
				r)				r)				r)				
blank	.25			1.01	.34			.23	.47			.15	.58			.131
1	.12	52	.52	.48	.14	57	.57	.09	.19	59	.59	.06	.23	60	.60	.052
2	.07	72	.72	.28	.09	73	.73	.06	.12	74	.74	.04	.14	75	.75	.031
3	.035	86	.86	.14	.04	87	.87	.02	.05	88	.88	.01	.05	91	.91	.011
5	.02	92	.92	.08	.02	93	.93	.01	.02	95	.95	.006	.01	98	.98	.002



Figure 2. The graph inhibition efficiency v/s concentration of inhibitor (%) at different time interval for copper in 0.5 M HCl.



Figure 3. Langmuir adsorption isotherm for copper at different time interval in 0.5 M HCl.



Figure 4. IR spectrum of BPEPM.



Figure 5. NMR spectrum of BPEPM.

CONCLUSION

The efficiency of synthesized Schiff base BPEPM for corrosion inhibition of copper metal in acidic media have been studies. Conclusions of study are:

- The inhibition efficiency of inhibitor increases with concentration.
- The inhibition efficiency increases according increasing immersion time exposure it mean it is effective over long range of time.
- The inhibitor obey Langmuir adsorption isotherm pattern during inhibition process.
- This Schiff base act as potential inhibitor for copper corrosion in 0.5M HCl medium.

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Corresponding author: Sanjay Kumar: Research Laboratory, Department of Chemistry, Govt. Lohia (PG) College, Churu, India Email: <u>sanjaysnkp@gmail.com</u>