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Evaluation of Schiff's bases synthesised from 2-hydrazinobenzimidazole as corrosion inhibitor of copper in H_2SO_4

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ABSTRACT

The corrosion inhibition effects of newly synthesised Schiff's bases from 2-hydrazinobenzimidazole for copper in 1N sulphuric acid was evaluated using weight loss and Tafel polarisaton method. The interaction of these molecules with the copper was studied by FTIR method. The inhibitive action of the Schiff's bases was due to their adsorption on the metal surface. The inhibitor efficiency was found to depend on the charge density on the atoms of the functional group. The Schiff's bases were found to be acting as anodic inhibitors

KEYWORDS

Schiff's base;
Corrosion inhibition;
Tafel;
Hydrazinobenzimidazole.

INTRODUCTION

Copper and its alloys are increasingly used in industries for their excellent heat and thermal conductivities and workability. However their efficiency decreases with time due to formation of scale over the surface. Periodical and regular cleaning is done to preserve their conductivity by using sulphuric acid as pickling agent. This leads to acidic corrosion of the metal which reduces the life time. Organic inhibitors are used to protect the surface from such corrosion. The inhibitor inhibits the corrosion by forming protective layer over the metal surface. Recent studies have suggested Schiff's bases to be effective corrosion inhibitor for copper and its alloys[1-7]. Schiff's bases are easily synthesized and can be modified accordingly.

The aim of this study is to synthesise Schiff bases 2-(benzimidazolyl-2'-amino) imino ethanone (HBIE), 2-(benzimidazolyl-2'-amino) imino-1,2-dimethyl ethanone (HBIME) from 2-hydrazinobenzimidazole (HB) and to evaluate their corrosion inhibition properties on copper in sulphuric acid medium by using weight loss method, electrochemical techniques.

EXPERIMENTAL

The copper metal used in this study was 99.9% pure. The working copper electrodes were cut into cylindrical rods and covered with araldite leaving 1 cm^2 area exposed after welding with copper wire. The exposed surfaces were ground with 150,320,400,600 and 1000 grade emery paper before each use. The electrodes were polished by 4/0 polishing paper and cleaned with acetone.

The Schiff's bases were synthesized as follows by using Merck/sd fine AR chemicals.

2-hydrazinobenzimidazole was synthesized by mixing 2-merceptobenzimidazole and hydrazine hydrate in ethanol medium and refluxed for 4 hours. White coloured crystals were formed which were recrystallised from ethanol (Figure 1). HBIE was synthesized by mixing alcoholic solution of HB and ethanolic solution of glyoxal and refluxed for 4 hours. A brick red precipitate was formed (Figure 2). HBIME was synthesized mixing alcoholic solution of HB and ethanolic solution of diacetyl and refluxed for 4 hours. A yellow coloured precipitate was formed (Figure 3). Both the compounds were recrystallised with ethanol before use. The compounds were analysed for C, H, N by using semi-micro combustion method for carbon and hydrogen and Kjeldahl's method for nitrogen (TABLE 1). The inhibitor solutions of 10 ppm,50 ppm and 100ppm in 1N sulphuric acid were prepared.

The Tafel polarization studies were carried out in electrochemical work station (CHI) using platinum wire as counter electrode and saturated calomel electrode

as reference electrode. The FTIR studies were done in Shimadzu-FTIR-8400S.

RESULTS AND DISCUSSION

The weight loss values for copper in 1N H_2SO_4 and for different concentrations of HBIE and HBIME after keeping for 12 hours are shown in TABLE 1. It shows that inhibitor efficiency increases with increase in inhibitor concentrations. The efficiency of HBIME molecules in inhibiting corrosion of copper in H_2SO_4 is found to be more than those of HBIE molecules.

The anodic and cathodic Tafel polarization curves for copper in 1N H_2SO_4 at 10, 50,100 ppm concentrations of HBIE are shown in Figure 4. The corrosion parameters are shown in TABLE 3. The results show that with increase in concentration of the inhibitor, the

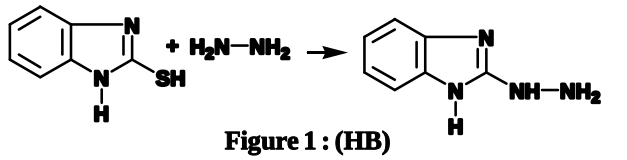

Figure 1 : (HB)

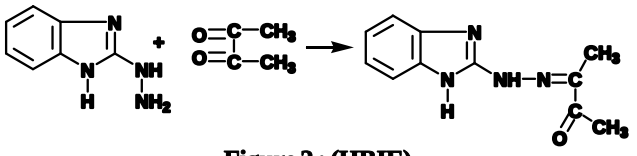

Figure 2 : (HBIE)

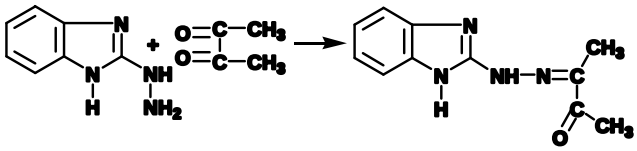

Figure 3 : (HBIME)

inhibition efficiency is increasing. The maximum inhibition efficiency is 86.9% for 100ppm of HBIE. The corrosion potential shifts in the positive direction indicating dominance of anodic inhibition by the molecules. Figure 5 shows the effect of increase of concentration of HBIME on inhibition efficiency. The parameters are shown in TABLE 3. The maximum efficiency is found to be 91.8% for 100 ppm of HBIME molecules. The positive shifts of corrosion potentials indicate predominance of anodic inhibition of HBIME molecules. Both the molecules inhibit corrosion by blocking the anodic sites on the metal surface by forming protective layer over it. This may involve transfer or share of charge from the molecules to the metal surface to form a coordinate type bonding. The presence of electron donating functional groups in the compound can increase the electron density on C=N group of the Schiff' bases[8]. Both molecules possess atoms with charge densities to coordinate with the metal. The inhibition efficiency of HBIME is found to be more than that of HBIE. This

TABLE 1 : Analytical data of inhibitors

Inhibitor	%C	%N	%H
HBIE	36.98	38.39	0.32
HBIME	35.57	45.57	0.24

TABLE 2 : Weight loss values

Inhibitor	Conc. (ppm)	Weight loss (gm.)	Inhibition efficiency (%)
1N H_2SO_4		0.0086	–
HBIE	10	0.0031	63.9
	50	0.002	76.7
	100	0.0012	86
HBIME	10	0.0026	69.8
	50	0.0015	82.6
	100	0.0008	90.7

may be due to presence of methyl groups in the molecules which increase the charge density on N- and O-atoms. As the electron density increases, the inhibition efficiency increases[9]. The increase in electron density enhances the corrosion inhibition efficiency characteristics of HBIME molecules.

The Langmuir adsorption isotherm is $\frac{\theta}{1-\theta} = ACe^{-2a\theta} = KC$, where θ = surface coverage, C= inhibitor concentration, α = molecular interaction and K= adsorption constant.

The above equation can be represented as $\frac{C}{\theta} = C + \frac{1}{K}$

The plots of C/ θ and C are given for HBIE (Figure 6) and for HBIME (Figure 7). The isotherms show good agreement with the experimental results. The K values for HBIE and HBIME are calculated from the isotherm and found to be $31.15x10^3$ and $40x10^3$ dm^3/mol respectively. The higher value for HBIME may be attributed to higher adsorption capability as compared to HBIE molecules[10]. The values of changes in adsorption free energy ΔG^0 are calculated from K values as per equation $K = e^{-\Delta G^{0/RT}}$ and are found to be -25.64kJ/mol for HBIE and -26.25kJ/mol for HBIME. The more negative value for HBIME can be attributed to more adsorption as compared to HBI

The FTIR spectra of the synthesized Schiff' bases and the compounds scrapped from the surface of copper are taken. This provides information on the mode of bonding between the metal and inhibitor molecules.2-hydrazinobenzimidazole exhibits bands at around 3230 cm^{-1} which can be assigned to symmetric and asymmetric stretching mode of vibration of NH_2 group overlapped by secondary NH_2 group. Bands at around 1250 and 1030 cm^{-1} may be assigned to new C-N and N-N stretching respectively. Formation of HBIE and HBIME from HB brings about significant changes in the spec-

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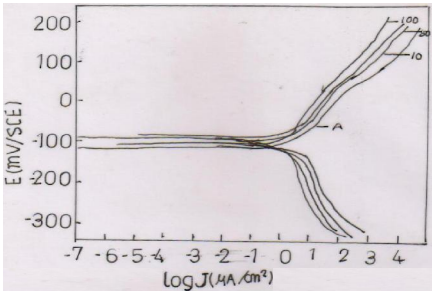

Figure 4 : Tafel curves for copper in 1N

TABLE 3 : Tafel polarsation parameters for copper in 1N H_2SO_4 with different concentrations of HBIE and HBIME

Inhibitor	Conc. (ppm)	E_{corr} (mV/SCE)	I_{corr} (μA/cm2)	Inhibition efficiency (%)
1N H_2SO_4		-116	6.1	--
HBIE	10	-98	2.1	65.5
	50	-91	1.3	78.7
	100	-109	0.8	86.9
HBIME	10	-93	1.8	70.5
	50	-88	1.0	83.6
	100	-107	0.5	91.8

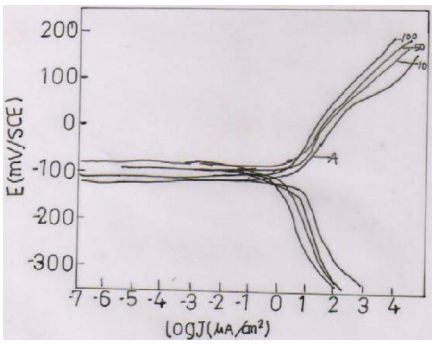

Figure 5 : Tafel curves for copper in 1N

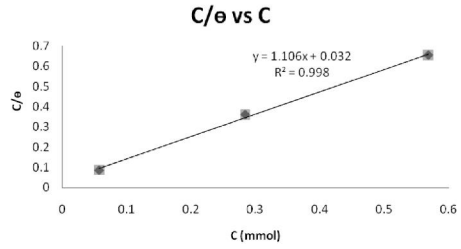

Figure 6 : Langmuir isotherm for HBIE

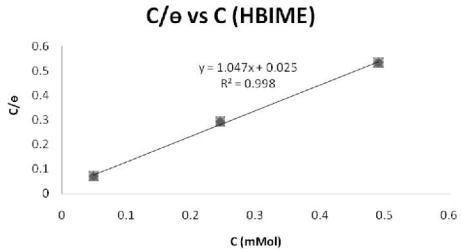

Figure 7 : Langmuir isotherm for HBIME

tra. The notable feature is the disappearance of bands due to NH_2 stretching and deforming vibration. Appearance of two new bands at 1670 and 1551 cm^{-1} may be due to new C=O and new C=N bonds in the inhibitor molecules. In the scrapped compound, a very broad band with center of gravity at around 3470 cm^{-1} indicates the presence of water molecules which may be coordinating with the metal. The broadness of the band may be due to intramolecular H-bonding. The position of band due to new $C=N_{cyclic}$ and new $C\text{-}N_{cyclic}$ with benzimidazole moiety remain unchanged pointing to their non participation in the bonding with the metal. The new C=N and C=O band has shifted by 10-20cm^{-1} in both the scrapped compound indicating bonding of inhibitor molecules with metal. This supported further by appearance of new bands in the lower frequency region. Two bands at 520 and 450 cm^{-1} may be assigned to new M=O and new M-N stretching vibration respectively.

CONCLUSIONS

Both the synthesized Schiff's bases have shown good inhibition properties for copper corrosion in 1N H_2SO_4 medium. The inhibition efficiencies are 91.8% and 86.9% for 100 ppm of HBIME and HBIE molecules. The inhibitive action may be attributed to adsorption of the molecules on the metal surface through O and N atoms. The adsorption process obeys the Langmuir's adsorption isotherm. The efficiency was found to very in accordance with charge density on the atoms of the molecules. The efficiencies were found to increase with inhibitor concentrations.

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