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Inhibition of corrosion of copper by substituted triazoles in 3.5% NaCl solution

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ABSTRACT

In the present investigation 3-methyl-4-amino-5-mercaptotriazole (Inh I) and 3-(2-hydroxyphenyl)-4amino-5-mercaptotriazole(Inh II) have been synthesized and studied as inhibitors for the corrosion of copper in 3.5 % NaCl solution . The inhibition efficiency of the compounds have been evaluated by weight loss and electrochemical polarization methods. The surface study was done by using SEM. The inhibitors appear to inhibit corrosion process through formation of protective film which was found to consist of Cu(I)-inhibitor complex, cuprous chloride, CuCl or $CuCl_2^-$ complex ion or both on the surface.

Keywords: Copper, corrosion inhibition, Polarization, SEM, sodium chloride solution.

INTRODUCTION

Due to its high electrical and thermal conductivity and good mechanical workability, copper is a material widely used in pipelines for domestic and industrial water utilities, including seawater, heat conductors, and heat exchangers [1]. In spite of the relatively noble potential of copper, its corrosion takes place at a significant rate in sea water and chloride environment [2]. It is generally accepted that anodic dissolution of copper in chloride environments is influenced by the chloride ions concentration. At chloride concentrations lower than 1 M, the dissolution of copper occurs through formation of CuCl, which is not protective enough and is converted to the soluble $CuCl_2^-$ by reacting with excess chloride ions, on the other hand, at concentrations higher than 1 M, higher cuprous complexes such as $CuCl_3^{2-}$ and $CuCl_4^{3-}$ are formed, in addition to the ones with fewer chlorides, such as CuCl and $CuCl_2^-$ [3].

It is generally believed that corrosion inhibitors effectively eliminate the undesirable destructive effects of aggressive media and prevent copper, dissolution. Organic compounds containing polar groups including nitrogen, sulphur, and oxygen and heterocyclic compounds with polar functional groups and/or conjugated double bonds, such as mercaptotriazole [4], imidazoles [5], cysteine [6], semicarbazides [7], thiosemicarbazide [8] and benzotriazole [9] have been reported to inhibit copper corrosion. The inhibiting action of these compounds is usually attributed to their interactions with the copper surface via their adsorption. Polar functional groups are usually regarded as being a reaction center by establishing the adsorption process [10].

In the present investigation, experiments have been performed to assess the inhibitive action of 3-methyl-4-amino-5-mercaptotriazole and 3-(2-hydroxyphenyl)-4amino-5-mercaptotriazole in 3.5% NaCl solution at 25^{o}C.

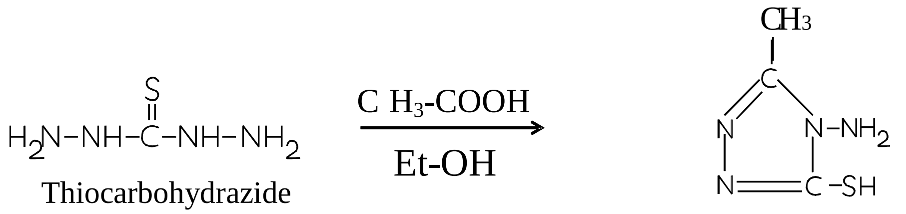
EXPERIMENTAL SECTION

Copper specimens taken for experiments were supplied by M/s Good Fellow Metals Ltd England(99.99% pure Cu). Sodium chloride (NaCl, Merck 99%), thiocarbohydrazide (Aldrich, 98%) benzoic acid (Merk,99%) and absolute ethanol (C_2H_5OH, Merk, 99.9%) were used as received. The samples for the weight loss and electrochemical polarization studies were of the size 3 cm × 2 cm × 0.1 cm and 1 cm × 1 cm × 0.1 cm, respectively. The samples were polished successively with 1/0 – 4/0 grade emery papers, washed with benzene followed by hot soap solution and finally with distilled water. They were degreased by immersing in acetone for 1-2 min, dried and stored in vacuum desiccator. The weight loss experiments were carried out in 500 ml corning glass beakers with lid containing 300 ml of 3.5% NaCl solution in static condition. The inhibition efficiencies were evaluated after a period of 120 h. using 20, 50, 100 and 150 ppm of compound.

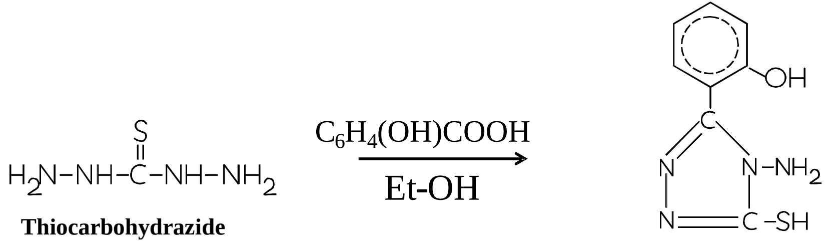
$$\% \text{ IE} = \theta \times 100$$

Where θ is the fraction of surface area covered by inhibitor, and $\theta=(a-b)/a$, where a is weight loss of the sample in absence of inhibitor and b is weight loss of sample in presence of inhibitor. After removing the specimen's from the electrolytes, they were washed thoroughly with distilled water, dried and then weighed. Mean of weight loss values of three identical experiments were used to calculate the inhibition efficiencies of the inhibitors. The electrochemical experiments were performed using a VoltaLab-10 electrochemical analyser containing Voltamaster 4.0 software. For potentiodynamic polarization experiments, the potential was scanned from -600 to 500 mV at a scan rate of 1 mV/s.

The inhibitors were prepared by refluxing a mixture of thiocarbohydrazide and carboxylic acid in 1:1 ratio in the presence of ethanol for 4 hours. The resulting clear solution was allowed to stand overnight in a capped round bottom flask during which time the product crystallized as a coarse off-white crust on the sides of the flask. The solid was collected by suction filtration and air dried to remove residual acid.



3-methyl-4-amino-5-mercaptotriazole (Inh I)



3-(2-hydroxyphenyl)-4amino-5-mercaptotriazole (Inh II)

For calculating %IE by electrochemical polarization method we use the formula-

$$\% \text{ IE} = \frac{I_0 - I_{inh}}{I_0} \times 100$$

where I_0 = Corrosion current in absence of inhibitor
I_{inh} = Corrosion current in presence of inhibitor

RESULTS AND DISCUSSION

1.1. Weight loss studies

The inhibition efficiency values of the inhibitors at various concentrations at 25°C calculated by weight loss ethod have been given in table I. It is evident from the data in the table that inhibition efficiencies (IEs) of the inhibitors increases with increase in concentration and becomes more or less constant at 200 ppm. Considering the potential dependent adsorption of the molecule, the effectiveness of the inhibitor can be correlated with the structure and size of inhibitor molecule.

Table 1 : Percentage inhibition efficiency (% IE) values calculated by weight loss method for Inh I and Inh II at 25^{0}C

Concentration(ppm)	Inh I	Inh II
50	61.24	64.42
100	84.36	88.92
150	90.42	94.56
200	91.18	95.12

Most of the organic compounds and metal complexes used as inhibitors have been found to inhibit corrosion process following the mechanism of adsorption. Assuming that this mechanism is valid for present molecules as well, IE of the inhibitor can be explained in term of the number of active centres for the adsorption, delocalized electron density and the projected surface area covered as a result of their adsorption. The inhibitors consist of nitrogen,and sulphur as active centres and delocalized π-electron density at phenyl and triazole ring causing a high % IE for the inhibitor. It may be noted that there does not exist any direct correlation between magnitude in increase in IE values and the number of expected sites of adsorption and size. This may be due to the fact that the number of active centres actually involved in adsorption may be different than the number of active centres present in the molecules owing to their geometry.The %IE of Inh II is greater than the %IE of Inh I due to +I effect of –OH group.

2.2 Potentiodynamic polarization studies

The electrochemical polarization behaviour of copper was studied in 3.5% NaCl solution containing different concentrations of the synthesized inhibitors. Fig.1,2 represent the electrochemical polarization behaviour of copper in 3.5% NaCl solution at 25^oC in absence and presence of different concentrations of the inhibitors Inh I and Inh II, respectively, at 25^oC. As reported earlier the anodic polarisation curve in absence of inhibitors exhibit Tafel region at lower applied potential extending to a peak current density (I_{peak}) due to the dissolution of copper into Cu^+ , a region of decreasing current until a minimum (I_{min}) is reached due to formation of CuCl and a region of sudden increase in current density leading to a limiting value (I_{lim}.) as a result of formation of soluble $CuCl_2^-$. The nature of polarisation curve in presence of the inhibitors resembles the curves in their absence with slight gradual shift towards lower current density at all the concentrations. Thus, the inhibitors may be considered to inhibit corrosion of copper by blanketing a part of the electrode surface due to formation of protective film of Cu(I)-inhibitors complex and polarizes the anode without affecting the basic mechanism of corrosion.

The decrease in I_{corr} , I_{peak} , and I_{min} values in presence of inhibitors is mainly due to the decrease in the chloride ion attack on the copper surface due to the adsorption of the inhibitors. The negative shift in the E_{corr} in presence of inhibitors on increasing the concentration of the inhibitors is due to the decrease in the rate of cathodic reaction. Moreover, the increase in the cathodic and anodic Tafel slopes (β_c and β_a) are related to the decrease in both the cathodic and anodic currents. This indicates that the the inhibitors are good corrosion inhibitos for copper in 3.5%NaCl solution and their inhibition efficiency increases on increasing their concentrations. At higher concentrations, the Tafel region almost vanishes completely and peak current density disappears in presence of the inhibitor. Therefore, the inhibitors may be considered to inhibit the corrosion process both through chemical adsorption via formation of complex at the surface of the copper. Fig. 1,2 show that addition of inhibitor significantly decreases the cathodic and anodic currents, with the corrosion potential ($E_{corr.}$) values slightly shifted in the negative direction. Corrosion parameters such as $E_{corr.}$, $I_{corr.}$, cathodic slope (β_c), anodic slope (β_a) and $k_{corr.}$ obtained from Fig. 1,2 are given in Table:2,3.

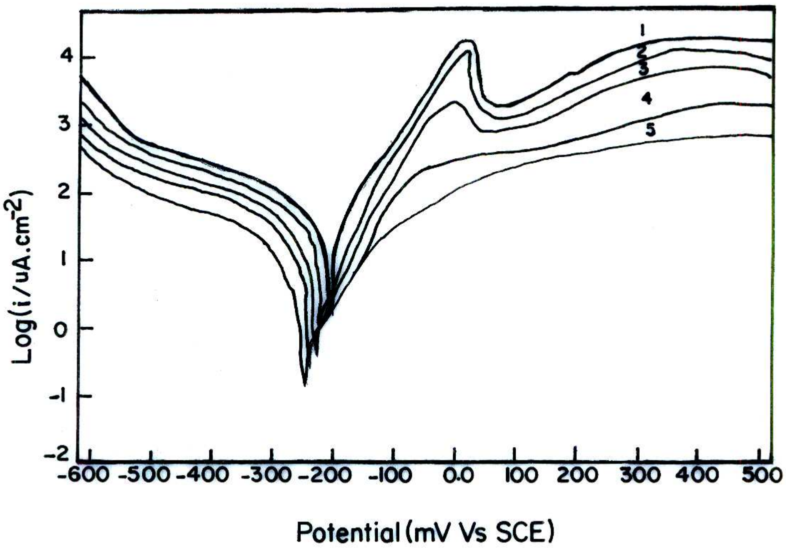


Figure 1: Potentiodynamic polarization curves for the copper electrode in 3.5%NaCl solution without (1), with 50 ppm (2), 100 ppm (3), 150 ppm (4) and 200 ppm (5) of Inh I at 25°C

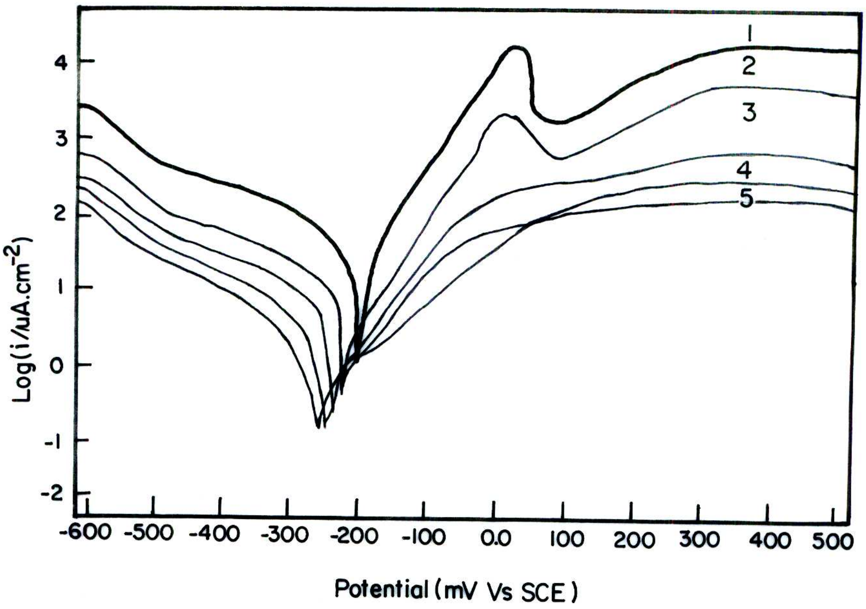


Figure 2: Potentiodynamic polarization curves for the copper electrode in 3.5%NaCl solution without (1), with 20 ppm (2), 50 ppm (3), 100 ppm (4) and 150 ppm (5) of Inh II at 25°C

Table 2: Corrosion parameters obtained from potentiodynamic polarisation curves shown in fig. 1 for copper electrode in 3.5% NaCl solution in the absence and presence of inhibitor

Concentration (ppm)	Parameters					
	E_{corr} (mV)	I_{corr} (μA cm^{-2})	β_c (mV dec^{-1})	β_a (mV dec^{-1})	k_{corr} (mpy)	% IE
0	-220	14.00	90	50	3.24	-
50	-235	5.32	95	60	0.71	62.54
100	-240	2.38	100	65	0.48	83.62
150	-245	1.26	115	70	0.29	91.36
200	-250	1.12	130	74	0.26	92.25

Table 3: Corrosion parameters obtained from potentiodynamic polarisation curves shown in fig. 2 for copper electrode in 3.5% NaCl solution in the absence and presence of inhibitor

Concentration (ppm)	Parameters					
	E_{corr} (mV)	I_{corr} (μA cm^{-2})	β_c (mV dec^{-1})	β_a (mV dec^{-1})	k_{corr} (mpy)	% IE
0	-220	14.00	90	50	3.12	-
50	-240	4.90	92	65	0.66	65.22
100	-245	2.38	96	70	0.36	87.85
150	-250	0.98	105	75	0.32	93.25
200	-255	0.84	110	80	0.22	94.36

The decrease in corrosion current ($I_{corr.}$), peak current (I_{peak}), minimum current (I_{min}) and rate of corrosion(k_{corr}) values are mainly due to the decrease in the chloride ions attack on the copper surface, which causes the decrease in Cu dissolution by absorption of the inhibitors molecules. Furthermore the increase in anodic and cathodic Tafel slopes (β_a and β_c) values are related to the decrease in the anodic and cathodic currents, which in turn limits the electrodissolution of copper.

The anodic dissolution of copper occurs through oxidation of metallic copper to cuprous ions

$$Cu \rightarrow Cu^+ + e^-$$

This in turn reacts with chloride ions from the solution to form CuCl.

The formed CuCl reacts with excess chloride ion in the solution to form cuprous chloride complex ($CuCl_2^-$) through which the dissolution of copper occurs .

$$CuCl + Cl^- \rightarrow CuCl_2^-$$

$$CuCl_2^- \rightarrow Cu^{2+} + 2Cl^- + e^-$$

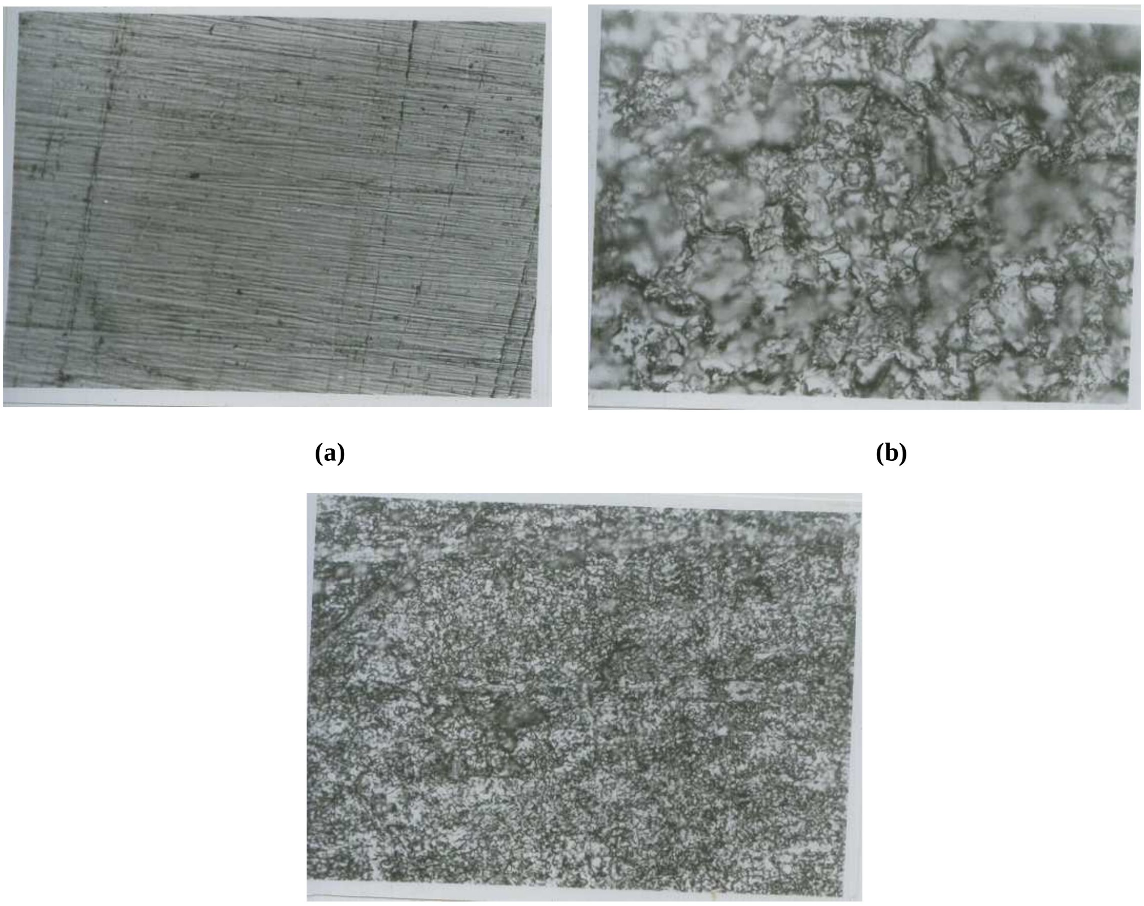
The cathodic reaction of copper in 3.5% NaCl solution is well known to be the oxygen reduction.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The inhibition efficiencies calculated from potentiodynamic polarisation measurement are in good agreement with the values obtained by weight loss method.

2.3 SEM study

Figures 3(a, b, c) show the micrographs for copper in 3.5%NaCl solution in absence and presence of 200 ppm of Inh II at 200X magnification. On comparing these micrographs, it appears that in the presence of inhibitor the surface of the test material has improved remarkably with respect to its smoothness. Smoothening of the surface would have been caused by the deposition of inhibitor molecules on it and thus, the surface is fully covered



(a) **(b)**

(c)

Fig. 3: Optical microphotographs of copper exposed to 3.5% NaCl solution (after polarization)

(a) Polished specimen
(b) In presence of 3.5% NaCl solution
(c) In presence of 200 ppm of Inh II

CONCLUSION

(i) Both the inhibitors act as efficient corrosion inhibitor for copper in 3.5% NaCl solution.
(ii) Both the inhibitors act as mixed inhibitors.

(iii) It is suggested from the results obtained from SEM that the copper corrosion is inhibited by the formation of a protective layer of Cu(I)-inhibitor complex on the copper surface in both the inhibitors.

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