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Archives of Applied Science Research, 2011, 3 (6):180-190  
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# Substituted dithiohydrazodicarbonamides as corrosion inhibitor for copper in 3.5% NaCl solution

M. Yadav\*, <sup>1</sup>Archana Yadav and <sup>2</sup>Sunita Yadav

\*Department of Applied Chemistry, Indian School of Mines University, Dhanbad, India

<sup>1</sup>Department of Chemistry, S.N.P.G. College, Azamgarh, India

<sup>2</sup>Department of Chemistry, S.G.R.P.G. College Dobhi, Jaunpur, India

## ABSTRACT

The inhibition of copper corrosion in 3.5% NaCl solution has been studied at 25°C using three inhibitors 1-phenyl-2,5-dithiohydrazodicarbonamide (Inh I), 1-p-methoxyphenyl-2,5-dithiohydrazodicarbonamide (Inh II) and 1-p-chlorophenyl-2,5-dithiohydrazodicarbonamide (Inh III). The inhibition efficiencies of these compounds have been evaluated by weight loss and electrochemical methods (Impedance spectroscopy and polarisation curves). The surface study was done by using SEM and ESCA techniques. The inhibition efficiencies of the inhibitors follow the sequence. Inh II > Inh I > Inh III. The inhibitors Inh I, Inh II and Inh III appears to inhibit corrosion process through formation of protective film which was found to consist of Cu(I)-inhibitor complex, cuprous chloride CuCl or CuCl<sub>2</sub><sup>-</sup> complex ion or both on the surface.

**Keywords:** Dithiohydrazodicarbonamides, Copper, Corrosion inhibition

## INTRODUCTION

Copper, despite being noble metal, corrodes significantly in water containing chloride ions. Extensive use of copper as a structural material in cooling systems of nuclear installation, automobiles, power plant, oil refineries, sugar factories [1-3] etc., has prompted a thorough investigation on the kinetics and mechanism of copper corrosion in water containing chloride ions with various amount of inhibitors added to it. Compounds like various derivatives of aminothiazoles[4], benzotriazoles[5-7], thioimidazoles[8], thiadiazoles[9], quinolines[10] dithiobiuretes[11] and thiosemicarbazides[12] are some examples of good inhibitors for this system. 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 [13-15] and heterocyclic

compounds with polar functional groups and/or conjugated double bonds [16] and [17] 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 [18]. However, the adsorption of an inhibitor on a metal surface depends on several factors [19], such as the nature and surface charge of the metal, the adsorption mode, the inhibitor's chemical structure, and the type of the electrolyte solution.

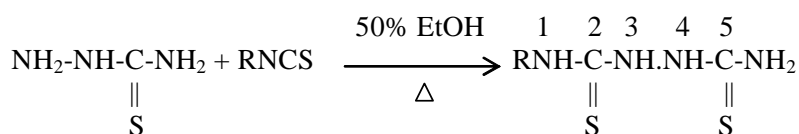
In the present work, the inhibitive effect of 1-phenyl-2,5-dithiohydazodicarbonamide (Inh I), 1-p-methoxyphenyl-2,5-dithiohydrazodicarbonamide (Inh II) and 1-p-chlorophenyl-2,5-dithiohydrazodicarbonamide (Inh III) in controlling the corrosion of copper in 3.5% NaCl solution has been studied using the weight loss method and electrochemical techniques. A suitable mechanism of corrosion inhibition has been proposed based on the result obtained from potentiostatic polarisation study, AC-impedance study and ESCA spectra.

### MATERIALS AND METHODS

Copper specimens taken for experiments were supplied by M/s Good Fellow Metals Ltd England (99.99% pure Cu). Thiosemicarbazide (Sigma-Aldrich, 95%). Sodium chloride (NaCl, Merck 99%), and absolute ethanol (C<sub>2</sub>H<sub>5</sub>OH, 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 electrolyte (3.5% NaCl by weight) in static condition. The inhibition efficiencies were evaluated after a period of 120 h. using 20, 50, 100 and 150 ppm of compounds Inh I, Inh II and Inh III using the formula

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

Where  $\theta$  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.

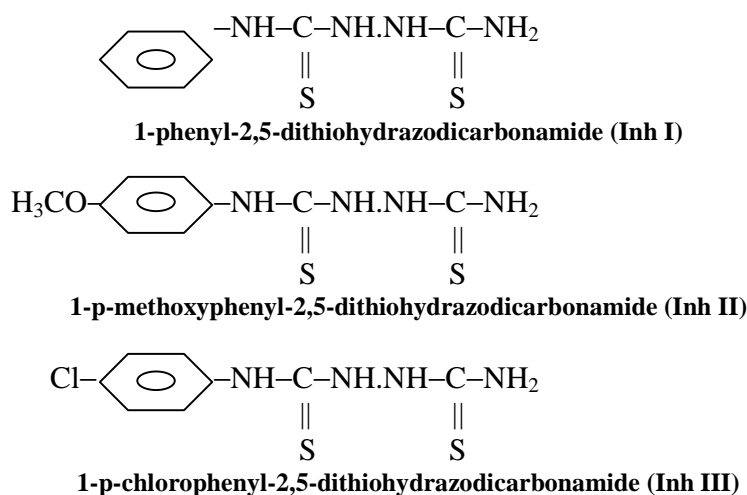


Where, R = phenyl-, p-methoxyphenyl- and p-chlorophenyl- groups.

The electrochemical experiments were performed using a VoltaLab-10 electrochemical analyser containing Voltmaster 4.0 software. For polarization experiments, the potential was scanned from -600 to 500 mV at a scan rate of 1 mV/s. Electrochemical Impedance Spectroscopy (EIS) measurements were performed between 100 kHz and 0.05 Hz frequency range. The compounds

Inh I, Inh II and Inh III were synthesized in the laboratory by refluxing thiosemicarbazide with appropriate arylisothiocyanates in 50% ethanol.

The structural formula of Inh I, Inh II and Inh III used in this study are shown below :



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

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

where  $I_0$  = Corrosion current in absence of inhibitor

$I_{\text{inh}}$  = Corrosion current in presence of inhibitor

% IE by impedance measurements were calculated by using the formula

$$\% \text{ IE} = \frac{R_{\text{ct(Inh)}} - R_{\text{ct}}}{R_{\text{ct(Inh)}}} \times 100$$

Where  $R_{\text{ct}}$  is the charge transfer resistance of the metal in absence of inhibitor and  $R_{\text{ct(Inh)}}$  is the charge transfer resistance in presence of inhibitor.

## RESULTS AND DISCUSSION

### 3.1 Weight loss study

The inhibition efficiency values of all the inhibitors at various concentrations at 25°C calculated by weight loss and polarisation techniques have been mentioned in table I.

It is evident from the data in the table that inhibition efficiencies (IEs) of all the inhibitors increases with increase in concentration and becomes more or less constant at 150 ppm. The IEs of these inhibitors follow the sequence:

$$\text{Inh II} > \text{Inh I} > \text{Inh III}$$

Considering the potential dependent adsorption of these molecules, the effectiveness of these inhibitors can be correlated with the structure and size of inhibitors molecules.

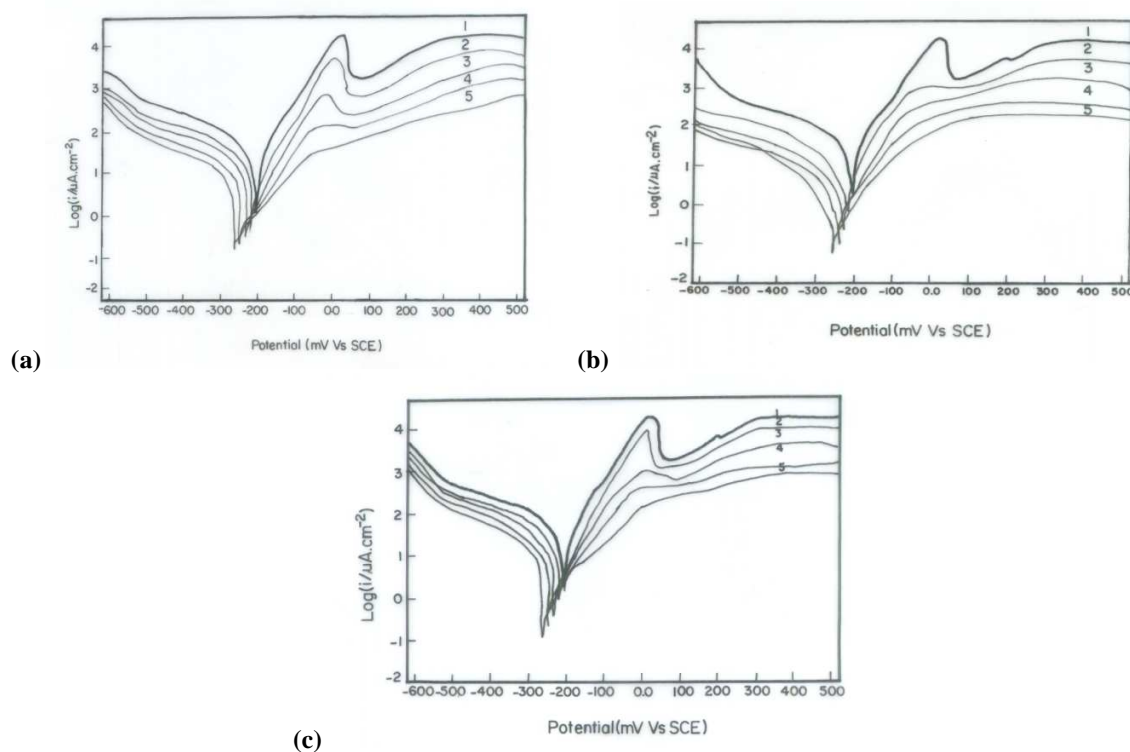
**Table 1: Percentage inhibition efficiency (% IE) values calculated by weight loss and polarization techniques for Inh I, Inh II and Inh III at 25°C**

Concentration	Inh III		Inh I		Inh II	
	% IE by wt. loss method	% IE by polarization method	% IE by wt. loss method	% IE by polarization method	% IE by wt. loss method	% IE by polarization method
20	57.24	57.82	71.18	70.56	77.24	78.42
50	63.12	63.72	76.52	78.13	84.36	84.82
100	69.32	69.68	85.14	85.62	90.42	91.66
150	69.46	70.02	86.43	86.52	91.62	92.18

Most of the organic compounds and metal complexes used as inhibitors have been found to inhibit corrosion process following the mechanism of adsorption [12]. Assuming that this mechanism is valid for present molecules as well, IE of these inhibitors 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 Inh I, Inh II and Inh III have nearly same size and number of active centres but Inh II show higher IE than the Inh I due to higher delocalised  $\pi$ -electron density at benzene ring. The delocalised  $\pi$ -electron density at benzene ring in case of Inh II is more than the Inh I due to electron donating nature of methoxy ( $-\text{OCH}_3$ ) group. The delocalized  $\pi$ -electron density at benzene ring in case of Inh III is less than the Inh I due to electron withdrawing nature of chloro ( $-\text{Cl}$ ) group. 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.

### 3.2 Electrochemical Polarization Study

The electrochemical polarization behaviour of copper was studied in 3.5% NaCl solution containing different concentrations of inhibitors, Inh I, Inh II and Inh III at 25°C. Fig. 1(b,c,a) represent the electrochemical polarization behaviour of copper in 3.5% NaCl solution at 25°C in absence and presence of different concentrations of inhibitor I, II and III respectively. As reported earlier (12), the anodic polarisation curve in absence of inhibitor exhibit Tafel region at lower applied potential extending to a peak current density ( $I_{\text{peak}}$ ) due to the dissolution of copper into  $\text{Cu}^+$ , a region of decreasing current until a minimum ( $I_{\text{min}}$ ) is reached due to formation of  $\text{CuCl}$  and a region of sudden increase in current density leading to a limiting value ( $I_{\text{lim}}$ ) as a result of formation of soluble  $\text{CuCl}_2^-$



**Fig. 1: Electrochemical polarisation of Cu in 3.5% NaCl solution in presence of (a) Inh I, (b) Inh II and (c) Inh III at 25°C**

The nature of polarisation curve in case of Inh I, Inh II and Inh III (Fig. 1a,b,c) resembles the curves in its absence with slight gradual shift towards lower current density at all the concentrations. Thus, Inh I, Inh II and Inh III 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)-inhibitor complex. In case of Inh I and Inh II (Fig. 1.a, b) although the nature of polarisation curves remains unaltered, the magnitude of shift towards lower current density is much larger than that for Inh III (fig.1c). The shift toward lower current density is higher for Inh II as compared to Inh I which is higher as compared to Inh III. The decrease in  $I_{\text{corr}}$ ,  $I_{\text{peak}}$ , and  $I_{\text{min}}$  values in presence of inhibitors are 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  $E_{\text{corr}}$  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 ( $\beta_c$  and  $\beta_a$ ) are related to the decrease in both the cathodic and anodic currents. This indicates that all the inhibitors are good corrosion inhibitors for copper in 3.5% NaCl solution and their inhibition efficiency increases on increasing their concentrations. Therefore, Inh I, Inh II and Inh III may be considered to inhibit the corrosion process both through chemical adsorption via formation of complex at the surface of the copper. Fig. 1(a-c) shows that addition of inhibitors Inh I, Inh II and Inh III significantly decreases the cathodic and anodic currents, with the corrosion potential ( $E_{\text{corr}}$ ) values slightly shifted in the negative direction. Corrosion parameters such as  $E_{\text{corr}}$ ,  $I_{\text{corr}}$ , cathodic slope ( $\beta_c$ ), anodic slope ( $\beta_a$ ) and  $k_{\text{corr}}$  obtained from Fig. 1(a-c) are given in Table (2,3,4).

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

Concentration (ppm)	Parameters					
	$E_{corr}$ (mV)	$I_{corr}$ ( $\mu\text{A cm}^{-2}$ )	$\beta_c$ (mV dec <sup>-1</sup> )	$\beta_a$ (mV dec <sup>-1</sup> )	$k_{corr}$ (mpy)	% IE
0	-220	14.00	90	50	3.24	-
20	-230	4.06	95	55	0.94	70.56
50	-240	3.08	110	62	0.71	78.13
100	-250	1.96	120	66	0.45	85.62
150	-260	1.82	125	72	0.42	86.52

**Table 3: Corrosion parameters obtained from potentiodynamic polarisation curves shown in fig. 1b for copper electrode in 3.5% NaCl solution in the absence and presence of inhibitor Inh II.**

Concentration (ppm)	Parameters					
	$E_{corr}$ (mV)	$I_{corr}$ ( $\mu\text{A cm}^{-2}$ )	$\beta_c$ (mV dec <sup>-1</sup> )	$\beta_a$ (mV dec <sup>-1</sup> )	$k_{corr}$ (mpy)	% IE
0	-220	14.00	90	50	3.24	-
20	-230	3.08	98	60	0.71	78.12
50	-240	2.10	115	68	0.48	84.92
100	-250	1.26	120	70	0.29	91.56
150	-260	1.12	130	72	0.26	92.12

**Table 4: Corrosion parameters obtained from potentiodynamic polarisation curves shown in fig. 1c for copper electrode in 3.5% NaCl solution in the absence and presence of inhibitor Inh III.**

Concentration (ppm)	Parameters					
	$E_{corr}$ (mV)	$I_{corr}$ ( $\mu\text{A cm}^{-2}$ )	$\beta_c$ (mV dec <sup>-1</sup> )	$\beta_a$ (mV dec <sup>-1</sup> )	$k_{corr}$ (mpy)	% IE
0	-220	14.00	90	45	3.24	-
20	-225	5.88	95	50	1.36	57.52
50	-230	5.04	100	55	1.16	63.82
100	-250	4.34	110	65	1.01	69.78
150	-250	4.20	120	70	0.97	70.12

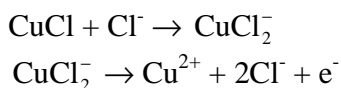
The decrease in corrosion current ( $I_{corr}$ ), peak current ( $I_{peak}$ ), minimum current ( $I_{min}$ ) and rate of corrosion ( $k_{corr}$ ) values are mainly due to the decrease in the chloride ions attack on the copper surface, which causes the decrease in Cu dissolution by absorption of the inhibitor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

The anodic dissolution of copper occurs through oxidation of metallic copper to cuprous ions [15]

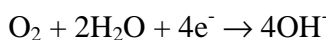


This in turn reacts with chloride ions from the solution to form CuCl [20].

The formed CuCl reacts with excess chloride ion in the solution to form cuprous chloride complex ( $\text{CuCl}_2^-$ ) through which the dissolution of copper occurs [21, 22].



The cathodic reaction of copper in 3.5% NaCl solution is well known to be the oxygen reduction [3, 20]



### 3.3 Electrochemical Impedance Study

To get further information concerning the inhibition process and to confirm the potentiodynamic polarization experiments, electrochemical impedance spectroscopic investigations of Cu in absence and presence of inhibitors in 3.5% NaCl solution were carried out. Electrochemical impedance is a powerful tool in the investigation of the corrosion and adsorption phenomenon. The impedance data of Cu, recorded in presence of 150 ppm of Inh I, Inh II and Inh III in 3.5% NaCl solution at 25°C as Nyquist plots are shown in fig. 2.

The Nyquist plots show depressed circular shape with their centres below the real axis. This behaviour is typical for solid metal electrodes that show frequency dispersion of the impedance data.

For a simple equivalent circuit consisting of parallel combination of a capacitor  $C_{dl}$ , and a charge transfer resistor  $R_{ct}$ , in series with a solution resistor  $R_s$ , the electrode impedance ( $Z$ ) in this case is represented by the mathematical formula

$$Z = R_s + \frac{R_{ct}}{1 + (2\pi f R_{ct} C_{dl})^\alpha}$$

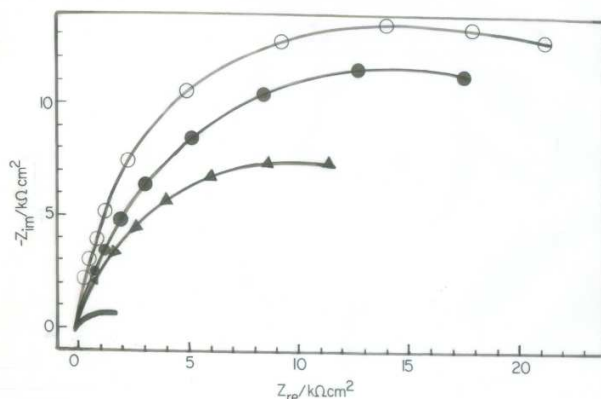
Where  $\alpha$  denotes an empirical parameter ( $0 \leq \alpha \leq 1$ ) and  $f$  is the frequency in Hz

The impedance spectra obtained experimentally were analysed using software provided with the electrochemical analyser. The impedance data of the copper electrode in presence of 150 ppm of Inh I, Inh II and Inh III were analysed using the equivalent circuit shown in fig. 3. The calculated equivalent circuit parameters for Cu in 3.5% NaCl solution at 25°C in presence of 150 ppm of Inh I, Inh II and Inh III are presented in Table 5. From the data in Table 5, it is clear that the value of  $R_{ct}$  increases on addition of the inhibitors, indicating that the corrosion rate decreases in presence of the inhibitors. It is also clear that the value of  $C_{dl}$  decreases on addition of inhibitors, indicating a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that all the inhibitors molecules function by formation of the protective layer at the metal surface.

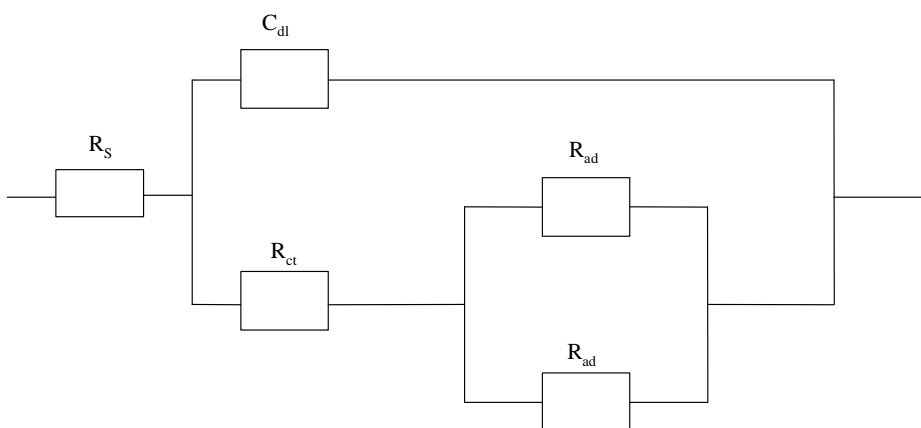
In order to confirm the potentiodynamic results, the corrosion inhibition efficiency (IEs) in presence of 150 ppm concentration of Inh I, Inh II and Inh III in 3.5% NaCl solution at 25°C was also calculated from the corresponding electrochemical impedance data according to

$$\% \text{IE} = \frac{R_{ct(\text{Inh})} - R_{ct}}{R_{ct(\text{Inh})}} \times 100$$

Where  $R_{ct}$  is the charge transfer resistance of the metal in absence of inhibitor and  $R_{ct(Inh)}$  is the charge transfer resistance in presence of inhibitor.



**Fig. 2:** Nyquist plot for Cu in 3.5% NaCl solution in presence of 150 ppm of ▲ Inh III, ● Inh I, ○ Inh II and — blank at 25°C



**Fig. 3:** Equivalent circuit model used in the fitting of the impedance data of Cu in 3.5%NaCl solution at 25°C

The values of  $IE_s$  are included in table 5 and represented graphically in fig.2. The inhibition efficiencies calculated from impedance data are very close to those obtained from potentiodynamic polarisation measurement. The results show the good agreement between measurements obtained from both techniques.

**Table 5:** Equivalent circuit parameters and inhibition efficiency for Cu in 3.5% NaCl solution in presence of 150 ppm of Inh I, Inh II and Inh III at 25°C

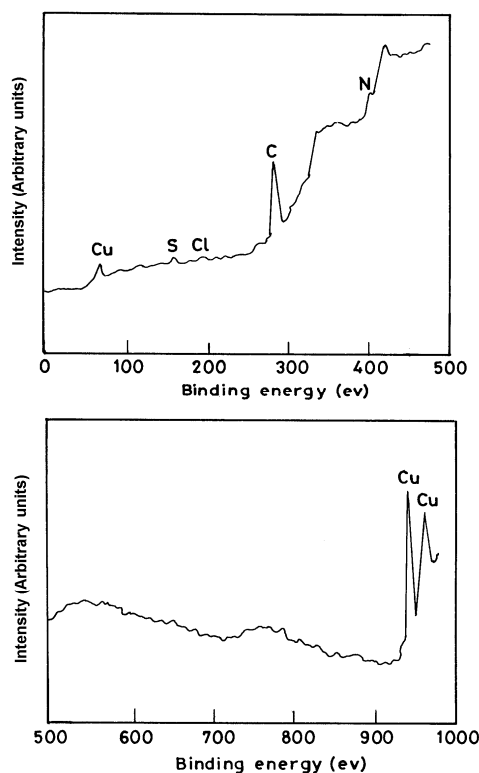
Compound	Concentration	$R_{ct}$ ( $K\Omega\text{ cm}^2$ )	$C_{dl}$ ( $\mu F\text{ cm}^{-2}$ )	%IE
	0	0.44	19.72	-
Inh III	150 ppm	1.52	16.24	71.12
Inh I	150 ppm	3.14	14.52	86.24
Inh II	150 ppm	6.28	12.64	93.18



### 3.4 Analysis of ESCA spectra

The ESCA patterns of the protective films formed on copper surface immersed in 3.5% NaCl solution in the absence and presence of inhibitor is shown in Figure 4. This ESCA pattern is interpreted with the help of data obtained from the literature [14] and experimental data taken from the Regional Sophisticated Instrumentation Centre, IIT Chennai, India for various elements exhibiting peaks at characteristic binding energy values.

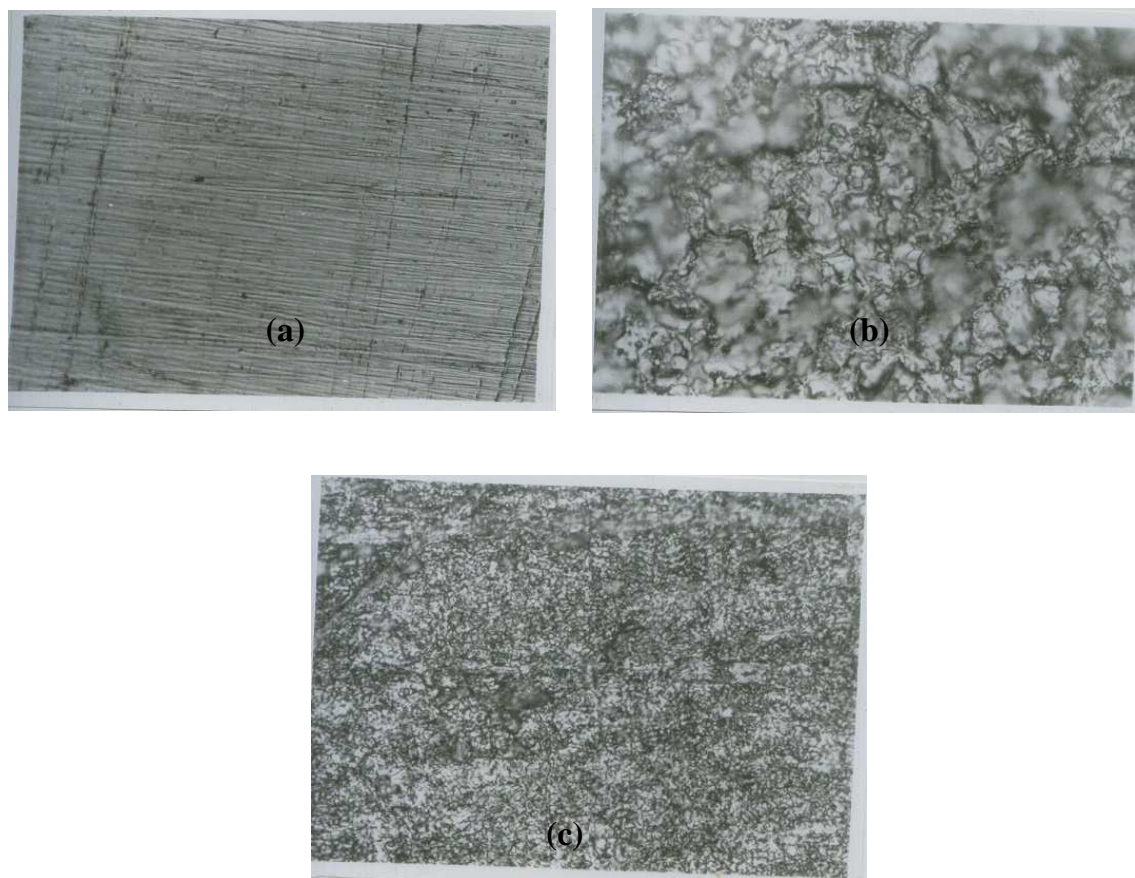
From the Figure 4, it is observed that in the presence of the inhibitor, the peak at 72 eV corresponds to 3p electrons of copper and the peaks at 934 eV and 950 eV are due to 2p electrons of copper. The peak at 198 eV is due to 2p electrons of chlorine. The peak at 286 eV is due to 1s electron of carbon atom. The observed peak at 162 eV is due to 2p electrons of sulphur atom. The peak at 401 eV is due to 1s electron of nitrogen atom. The presence of all the elements present in the inhibitor at the surface of the metal suggest the adsorption of the inhibitor and formation of Cu(I)-inhibitor protective layer at the surface of the metal.



**Figure 4:** ESCA pattern of the surface film formed on copper immersed in 3.5% NaCl solution in the presence of 150 ppm of the inhibitor Inh II at 25°C.

### 3.4 SEM study

Figures 5(a, b, c) show the micrographs for copper in 3.5% NaCl solution in absence and presence of 150 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. Smoothing of the surface would have been caused by the deposition of inhibitor molecules on it and thus, the surface is fully covered.



**Fig.5:** SEM image of copper (a) Polished sample (b) Exposed to 3.5% NaCl solution (c) In presence of 150 ppm of Inh II

### CONCLUSION

- (i) All the three compounds Inh I, Inh II and Inh III act as efficient corrosion inhibitor for copper in 3.5% NaCl solution.
- (ii) % IE of Inh I can be increased or decreased by a suitable substitution.
- (iii) Inh II shows appreciably higher efficiency than the Inh I and Inh III. due to presence of electron donating methoxy( $-\text{OCH}_3$ ) group.
- (iv) Inh III shows least inhibition efficiency due to presence of electron withdrawing chloro( $-\text{Cl}$ ) group.
- (v) The percentage inhibition efficiencies of these inhibitors follow the order  $\text{Inh II} > \text{Inh I} > \text{Inh III}$
- (vi) All the inhibitors act as mixed inhibitors.
- (vii) EIS measurements show that charge transfer resistance increases in presence of inhibitors.
- (viii) It is suggested from the results obtained from SEM and ESCA experiments that the copper corrosion is inhibited by the formation of a protective layer of Cu(I)-inhibitor complex on the copper surface.

**Acknowledgement**

Financial assistance from Indian School of Mines, Dhanbad, India, under the “Faculty Research Scheme” to M. Yadav is gratefully acknowledged.

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