

# Self Assembled Monolayers (Sams) of Methimazole on Copper in Corrosion Protection

A Rajalakshmi Devi, S. Ramesh, V. Periasamy

**Abstract-** Self assembled monolayers (SAMs) are formed on copper using Methimazole, under suitable conditions. Corrosion behaviour of copper is studied in neutral medium of 300 ppm aqueous sodium chloride solution using weight loss followed by electrochemical (impedance, potentiodynamic polarization), cyclic voltammetric studies. With the high charger transfer resistance, an efficiency of 95% is observed. The protective film formed on the surface is characterised by water contact angle measurements, FT-IR, SEM/EDX, and AFM studies. Potentiodynamic polarization studies have shown that SAMs control both anodic and cathodic reactions, but cathodic reactions more predominantly and behave as a mixed inhibitor. The surface film formed is found to be stable. The presence of nitrogen and sulphur in the inhibitor molecules on the metal surface due to chemisorption is analysed using EDX.

**Keywords:** Corrosion inhibition, SAMs, Methimazole.

## I. INTRODUCTION

The corrosion of copper and other metals occur usually when they are exposed to air. Copper is also exclusively used for piping and delivery of water for marine industries, which mainly contains sodium chloride. The high concentration of chloride ions severely leads to corrosion of copper. Various strategies have been applied to address the growing need for inhibition of copper corrosion. One of the most efficient approaches for protecting copper against aggressive attack is the formation of ultrathin films using SAMs. Corrosion inhibition of copper can be achieved by modifying its surface to form self-assembled monolayers using suitable organic inhibitors that contain mainly nitrogen and sulphur atoms which can adhere easily to the metal surface. The strong chemical interaction between sulphur atoms and the metallic surface leads to the formation of chemisorbed organic films. Kondoh et al investigated alkanethiolate monolayers on Cu(100) and found that sulphur atom in the thiolate occupied the 4-fold hollow site of the unreconstructed Cu(100) surface<sup>1</sup>. SAMs of organosulphur compounds are expected to function as a barrier to prevent the permeation of corrosion accelerants such as moisture and electrolyte into the copper substrate, thereby improving the corrosion resistance of copper<sup>2-5</sup>.

The aim of the present study is to investigate the ability and nature of SAMs of Methimazole on copper surface in sodium chloride environment in resisting corrosion using Gravimetry, impedance, potentiodynamic polarisation, CV, SEM/ EDX, Water contact angle measurements and AFM studies.

## II. EXPERIMENTAL PROCEDURE

### 2.1. Chemical and Method

A 99.99% pure AR grade Methimazole chemical is obtained from Sigma-Aldrich. (GR) grade ethanol is used as a solvent for preparing imidazole solution of required concentrations. The electrolyte solution is prepared using triple distilled water and analytical grade of (Merck) sodium chloride.

### 2.2. Sample preparation and SAM modification

The AR grade sigma-Aldrich make 99.99% pure chemical Methimazole is used to modify copper surface, in the formation of self-assembled monolayers. According to the literature, very lowest concentration<sup>6,7</sup> of the inhibitor substance can be effective in modifying the surface and the compound used in organic medium enhances the adsorption of nitrogen and sulphur, to the metal surface, Methimazole in ethanol medium is used. Hence, a solution of suitable concentration of 15 ppm Methimazole is used to modify the metal surface, in forming self-assembled monolayer. The copper specimens<sup>8</sup> of 3 × 1.5 cms are used. The metal plates are etched with HNO<sub>3</sub> and cleaned to mirror finish using emery sheets of grade 1 to 6 and then degreased with acetone<sup>9</sup>. The cleaned, degreased specimens are immersed in the inhibitor solution for about 24 hours, in room temperature. The specimens are weighed before and after immersion in the inhibitor solution. The surface modified specimens and pre-treated pure copper specimens are immersed in neutral aqueous medium of concentration of 300ppm sodium chloride for about 3 days and weighed for Gravimetry studies<sup>10</sup>. The surface protective film formed on the metal surface is visible for naked eye and the film remains the same even in neutral medium. The formation of SAMs can be classified in two steps,

Revised Manuscript Received on 30 May 2015.

\* Correspondence Author

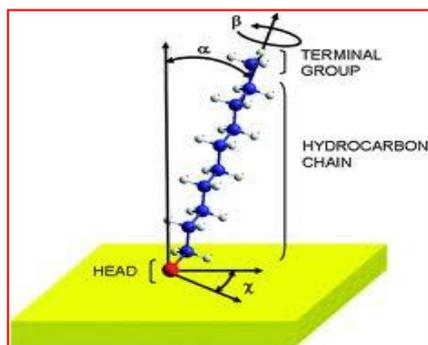
A. Rajalakshmi Devi, Department of Chemistry, The Gandhigram Rural Institute, Deemed University, Gandhigram 624 302 - India

S. Ramesh, Department of Chemistry, The Gandhigram Rural Institute, Deemed University, Gandhigram 624 302 - India

V. Periasamy, Department of Chemistry, The Gandhigram Rural Institute, Deemed University, Gandhigram 624 302 - India

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an open access article under the CC-BY-NC-ND license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

# Self Assembled Monolayers (Sams) of Methimazole on Copper in Corrosion Protection



as discussed by Rondelez et al<sup>11</sup>, the first step is the fast adsorption of molecules on the metal substrate and the second one being the slow re-arrangement of molecules to form a dense monolayer. The aqueous solution for neutral medium is prepared using analytical grade reagent and triple distilled water.

## 2.3. Electrode Preparation

A copper rod of same 99.99% purity with cross-sectional area of 1cm<sup>2</sup> embedded in epoxy resin leaving its square cross-section is used for electrochemical measurements. The copper electrode to be used is cleaned to mirror finish using various grade emery sheets and degreased with acetone. A dense and stable SAMs can be formed for an immersion time of 24 hours with a lowest concentration of 15 ppm of Methimazole inhibitor solution<sup>6,7</sup>.

## 2.4. Weight loss method

The rectangular copper specimens of dimension 3cm of length and 1.5cm width with a thickness of about 0.5 cm are used for weight loss studies. The specimens are etched with nitric acid to remove the oxidation products if any and polished to mirror finish using emery sheets of grade 1 to 6 and degreased with acetone. The specimens are weighed before and after immersion at the room temperature, using an analytical balance of precision 0.1 mg. The weighed samples are immersed in 100 ml solution of Methimazole for 24 hours at room temperature. Then the SAMs coated copper plates are washed with ethanol<sup>9</sup>. The washed plates and pretreated pure copper plates are immersed in 100 ml of 300 ppm sodium chloride solution for 3 days and then washed with ethanol, dried and weighed. The inhibition efficiency of SAMs covered copper to that of bare copper per day per dm<sup>2</sup> is calculated using the formula,

$$I.E. = (\Delta W - \Delta W_1) \times 100 / \Delta W,$$

Where  $\Delta W$  and  $\Delta W_1$  are the decrease in weights of bare copper plate and SAMs covered copper plate.

## 2.5. ELECTROCHEMICAL STUDIES

### 2.5.1. Potentiodynamic Polarization

The potentiodynamic polarization studies are carried out using copper electrodes of surface area 1cm<sup>2</sup>. A conventional three electrode cell consisting of SAMs modified copper immersed in the solution of 15 ppm concentration for a period of 24 hours as working electrode, Platinum as counter electrode and saturated calomel as reference electrode are used. Polarisation studies are carried out using CHI76D electrochemical analyser. The polarization curves are recorded in the potential range of -

200V to +500V Vs SCE, at a scan rate of 0.01 mV/s. The inhibition efficiency is calculated using the formula,

$$I.E. (\%) = (i_{\text{corr}} - i_{\text{corr}}^1) \times 100 / i_{\text{corr}},$$

Where  $i_{\text{corr}}$  and  $i_{\text{corr}}^1$  are the corrosion current densities of bare copper specimen and SAMs covered copper specimens respectively.

### 2.5.2. AC Impedance

AC impedance studies are carried out in a three electrode cell assembly using computer controlled CHI76D analyser, using SAMs covered copper as working electrode, saturated calomel as reference electrode, where both should be kept nearby and Platinum electrode as counter electrode, after an immersion for half an hour. The impedance measurements are carried out at the open-circuit potential in the frequency range from 600 kHz to 10m Hz. The charge transfer resistance(R) and double layer capacitance ( $C_{dl}$ ) are determined from Nyquist plots. The inhibition efficiency is calculated using charge transfer resistance values.

$$I.E. (\%) = (R_t - R_t^1) \times 100 / R_t$$

Where,  $R_t$  &  $R_t^1$  are the charge transfer resistance and resistance of SAMs covered copper specimen and bare copper specimen respectively.

### 2.5.3. Cyclic Voltammetry

Cyclic Voltammetric studies are carried out in aqueous 300 ppm NaCl solution after an immersion for half an hour in the potential range of -0.8 V to +0.2 V. A three cell electrode assembly is used at different sweep rates of 15, 30, 45, 60 and 120 mV/s for two sweep segments at the scan rate of 0.1 mV/s. In order to study the stability of the SAMs formed, the CV experiments are carried out for 15 cycles at the constant sweep rate of 0.1mV under the same potential range of -0.8 V to +0.2 V.

## 2.6. SURFACE CHARACTERISATION STUDIES

### 2.6.1. Fourier Transform Infra-red spectroscopic study

In order to investigate the binding elements on the SAMs covered copper specimens, the transmittance of the FT-IR spectra are recorded between 4000 and 400 cm<sup>-1</sup> with a resolution of 4cm<sup>-1</sup>, using JASCO 480 PLUS spectrophotometer, in a single reflection mode for bare copper and SAMs covered copper specimens. Bare copper and Methimazole (SAMs) covered copper specimens are mounted on the reflection accessory and the plane polarized light is incident from the surface normal.

### 2.6.2. Scanning Electron Microscopic Analysis

The dense ordered self-assembled monolayer modified metal substrate, which offers very high inhibition efficiency (due to the chemisorption of Methimazole in ethanol through nitrogen and sulphur) in aqueous 300 ppm sodium chloride solution is investigated using scanning-electron microscopic studies. The instrument used is VEGA3 TESCAN available in the Department of Chemistry, Gandhigram Rural Institute, Gandhigram.

### 2.6.3. Energy Dispersive X-ray Analysis

The copper specimens are immersed in the inhibitor solution of Methimazole for SAMs formation for 24 hours. After 24 hours, the specimens are taken out rinsed with ethanol and dried. The dried samples are immersed in aqueous solution of 300 ppm NaCl for three days and then rinsed with ethanol and dried. The nature of the film formed on the surface of the metal specimens are analysed by EDX. The protective films formed on the metal surface are recorded using VEGA 3 TESCAN instrument in order to detect the elemental peaks of nitrogen, sulphur present in SAMs or ions that cause corrosion, by diffusion.

### 2.6.4. Contact-angle measurements

To analyze if the self-assembled monolayers film formed on the copper metal surface is hydrophobic or hydrophilic in resisting corrosion, water contact angle measurements are done using sessile water drop method using Data Physics OCA series, available in the Department of Chemistry, CECRI, Karaikudi.

### 2.6.5. Atomic force microscopic study

Surface morphology such as the thickness of the self-assembled monolayers formed on the metal substrate which is responsible for corrosion inhibiting reaction can be studied using atomic force microscopic studies, using contact cantilever mode. The studies are made using Park systems' XE 100 with a scanning resolution of  $4096 \times 4096$  pixels and a scanning speed of N/A, with Z range of 12  $\mu\text{m}$  or 25  $\mu\text{m}$ , available in the Department of Chemistry, IIT, Madras.

## III. RESULTS AND DISCUSSION

As discussed earlier, the formation of Self-Assembled Monolayers on the metal substrate follows a two step process, the first step being a fast adsorption step and the second being the rearrangement step. The self-assembled monolayers organize themselves one above the other by Vander waals' force of attraction and the head group (sulphur) attaches with the metal substrate by chemisorption. To obtain densely ordered SAMs, the metal substrate is pre-treated, using  $\text{HNO}_3$  for a few seconds, then polished to mirror finish using different grades of emery sheets and degreased with acetone at room temperature. As already discussed, ethanol is chosen as the solvent with an immersion time of 24 hrs. The optimum concentration of Methimazole and the immersion period are confirmed through impedance studies.

### 1. Effect of concentration of imidazole film:

As reported in the literature, well ordered dense SAMs can be formed with an immersion period of more than 20 hours. The results of the present study show that an immersion period of 24 hours enhances the formation of the protective film. Hence an immersion period of 24 hours is chosen initially and imidazole films are formed on the copper substrate at various concentrations of Methimazole from 5 ppm to 20 ppm. Impedance studies carried out in aq. 300 ppm sodium chloride solution after an immersion of 24 hrs in the inhibitor solution & Nyquist plots are shown in **figure 1**. The equivalent circuits that fit best with the impedance plots are shown in **figure 6**. The  $R_{ct}$  value for 15 ppm imidazole concentration is found to be the maximum.

Hence, imidazole of 15 ppm concentration is chosen as the optimum concentration to form SAMs, which show maximum inhibition efficiency in protecting the metal surface by preventing diffusion of chloride ions from the solution and the diffusion of  $\text{Cu}^+$  ions from the metal surface to the solution. The impedance parameters are shown in **table 4**. The charge transfer resistance value is found to be the maximum as  $27.94 \text{ K}\Omega \text{ cm}^2$ , for inhibitor concentrations of 10 ppm, with much decrease in  $C_{dl}$  value as  $0.00066 \mu\text{F cm}^2$  and 'n' value of 0.88, which reveal the dense protective film formation on copper surface.

### 3.1.1. Effect of immersion period:

The corrosion mechanism of the copper electrode modified by SAMs in sodium chloride can be interpreted by the reaction models shown in **figure 6** below. In sodium chloride solution, the electrochemical corrosion of copper substrate can occur when both oxygen molecules and chloride ions reach the bare copper surface through the defects within SAMs. As the oxygen concentration in the sodium chloride solution is low and comparatively its diffusion co-efficient is small, the diffusion of oxygen from the bulk solution to the bare copper surface is much lower than diffusion of chloride ions. Therefore, imidazole SAMs are relatively stable and can strongly protect the copper substrate from corrosion in sodium chloride solution. The increase in  $R_{ct}$  value after 1 hour is considerably higher and from 4 to 6 hours immersion, it remains the same, hence the SAMs formed is found to be stable within 4 hours of immersion in sodium chloride solution, which is shown in **figure 8.a.** and the results are tabulated in **table 6**.

## 3.2. Corrosion protection of SAMs film

### 3.2.1. Weight loss Studies

The inhibition efficiency of the corrosion rates is expressed in  $\text{mg/dm}^2/\text{day}$ . The specimens are weighed before immersing them in the inhibitor solution of concentrations 5 to 30 ppm and after the formation of SAMs on the specimen, i.e, after a period of 24 hour immersion, the specimens are taken out, rinsed with ethanol solution, dried and weighed. These weighed samples after SAMs formation and the pre-treated pure copper specimens are immersed in neutral medium of 300 ppm aq. Sodium chloride solution for a period of three days and then rinsed with ethanol, dried and weighed. The inhibition efficiencies of the SAMs covered specimens in neutral medium of 300 ppm NaCl solution are calculated using I.E. =  $(\Delta W - \Delta W_1) \times 100 / \Delta W$ , Where  $\Delta W$  and  $\Delta W_1$  are the decrease in weights of bare copper plate and SAMs covered copper plate. The same have been repeated for a period of 10 day immersion along with the inhibitor in aq. 300 ppm sodium chloride solution and the results are tabulated below in **table 2**. The inhibition efficiencies found to vary with the variation in concentration and the corrosion rate of the metal specimens as it depends on the surface area of the specimens. SAMs covered copper is found to have an efficiency of 96% from the data shown in the table below.

## Self Assembled Monolayers (Sams) of Methimazole on Copper in Corrosion Protection

S. No.	Conc. (ppm)	Difference in wt.(gm)	C. Rate (mdd)	IE (%)
1.	5	0.0013	3.288	82
2.	10	0.0003	.7581	96
3.	15	0.0003	0.7184	96
4.	20	0.0004	0.9676	95
5.	25	0.0007	1.7570	90
6.	30	0.0011	2.7241	85

**Table 1. Corrosion rate from weight loss studies for a period of 3 day immersion**

S.No.	Conc. (ppm)	Loss/increase in wt.(gm)	C.Rate (mdd)	IE (%)
1.	5	0.0027	2.395	87
2.	10	0.0039	2.939	84
3.	15	0.0031	3.885	79
4.	20	0.0029	3.1781	82
5.	25	0.0045	3.304	82
6.	30	0.00185	2.733	85

**Table 2. Corrosion rates from weight loss studies for a period of 10 day immersion** Corrosion rate is calculated using the formula below:

$$\text{Loss in wt. (mg)}$$

$$\text{Surface area of specimen (dm}^2\text{)} \times \text{period of imm. (days)}$$

Whereas the surface area in turn is calculated using,

$$\text{SA (dm}^2\text{)} = 2 [(L \times B + B \times T + L \times T) - 3.142R (R-T)] 0.01,$$

Where 'L' the length, 'B' the breadth, 'T' the thickness of the copper specimens and 'R' the radius of the hole in the specimens respectively and the results obtained from weight-loss studies are in good agreement with the results obtained from impedance and polarization studies.

### 3.2.2. Potentiodynamic polarization studies

The potentiodynamic polarization curves for bare copper and SAMs covered copper with Methimazole, for 24 hour immersion in neutral medium of concentration range of 100 – 300 ppm sodium chloride, for an immersion of half an hour are shown in **figure 10.b<sup>1</sup>**. The corrosion current densities ( $I_{\text{corr}}$ ) are determined from the polarization curves obtained by Tafel extrapolation method. SAMs formed on the surface of the copper act as a barrier for the diffusion of

corrosive elements like chlorine and oxygen to the cathodic sites. With the increase in sodium chloride concentration,  $I_{\text{corr}}$  values are increased for both bare and SAMs covered copper. On comparison with bare copper in sodium chloride solution, lower  $I_{\text{corr}}$  values are obtained for SAMs covered copper in sodium solution for all concentrations. The results are shown in **table 8**. The corrosion inhibition efficiency of SAMs covered copper is found to be 95 %. These results are in good agreement with impedance studies and found good correlation with the results obtained from weight loss studies. For 5 ppm to 20 ppm concentration, the corrosion potential ( $E_{\text{corr}}$ ) for SAMs covered copper shifts more towards negative side and is found to be much lower than bare copper, which is shifted more towards cathodic side, while the shift in anodic slope is very less. The inhibition efficiencies of SAMs covered copper are in the range of 91-95 % within the concentration range studied. For e.g., the corrosion potential for bare copper is found to be +3 mV and SAMs covered copper is found to be -56 mV, which is shifted more towards cathodic side. The corrosion current densities for bare copper and SAMs covered copper in 300 ppm sodium chloride solution are found to be 125.4  $\mu\text{A}$  and 6.357  $\mu\text{A}$  respectively. The anodic and cathodic tafel slopes for bare in 300 ppm sodium chloride solution are found to be 192.38 mV/decade and 189.86 mV/decade respectively. For SAMs covered copper, it is found to be 182.98 mV/decade and 281.61 mV/decade respectively. This shows that SAMs control both anodic and cathodic reactions, but cathodic reaction to a larger extent. The anodic reaction is given by the dissolution of copper into  $\text{CuCl}$  and  $\text{CuCl}_2^-$  and the dissolution is determined by the rate of diffusion of soluble  $\text{CuCl}_2^-$  species.<sup>2</sup> The presence of sulphur and nitrogen in the metal surface in SAMs suppress the formation of  $\text{CuCl}$  or in other words the diffusion of  $\text{CuCl}_2^-$  species from the electrode surface into the bulk solution is prevented, thus controlling the anodic reaction which is explained by the deviation in the anodic peak current and the deviation in the cathodic current peak explains the cathodic reduction of cuprous oxide. Thus, there is a huge decrease in corrosion current, which proves that the SAMs formed inhibit copper from getting corroded. Thus, inhibition efficiency is calculated using the formula,

$$\text{I.E (\%)} = (i_{\text{corr}} - i_{\text{corr}}^1) \times 100 / i_{\text{corr}}$$

Where  $i_{\text{corr}}$  and  $i_{\text{corr}}^1$  are the corrosion current densities of bare copper specimen and SAMs covered copper specimen respectively and which is found to be 95% as said earlier above.

**Table 3. Corrosion parameters obtained by potentiodynamic polarization studies of bare and SAMs covered copper in aq. 300 ppm NaCl solution at different concentrations of inhibitor**

Inhibitor	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$b_a$ (mV/decade)	$b_c$ (mV/decade)	IE (%)
Bare copper	+3	125.4	192.38	189.86	-
MI 5 ppm	-22	22.23	189.93	257.66	82
10 ppm	-57	5.651	200.09	287.10	96
<b>15 ppm</b>	<b>-56</b>	<b>6.357</b>	<b>182.98</b>	<b>281.61</b>	<b>95</b>

20 ppm	-38	7.815	188.07	269.68	94
--------	-----	-------	--------	--------	----

Table 4. Impedance parameters of bare and SAMs covered copper in aq. 300 ppm sodium chloride solution at different concentrations of inhibitor

Conc. (ppm)	$R_{ct}$ ( $K\Omega\text{ cm}^2$ )	Cdl ( $\mu\text{F cm}^2$ )	n	IE (%)
Bare copper	2.56	0.044	0.35	-
5	23.14	0.0057	0.86	89
10	8.7	0.0041	0.61	71
15	35.75	0.0002	0.88	93
20	27.57	0.0004	0.87	91

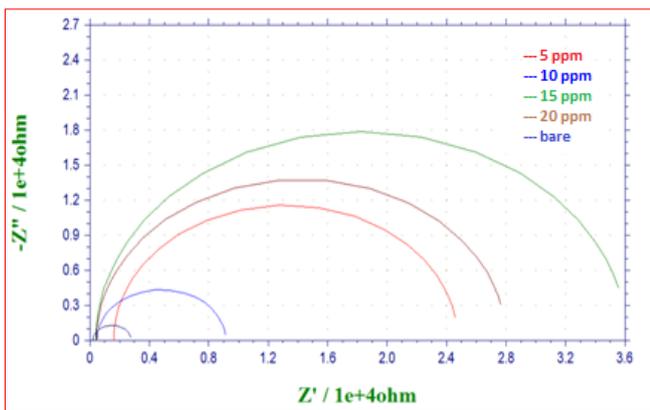


Figure 1. Nyquist plots of bare and SAMs covered copper of conc. 5 to 20 ppm in aq. 300 ppm sodium chloride solution

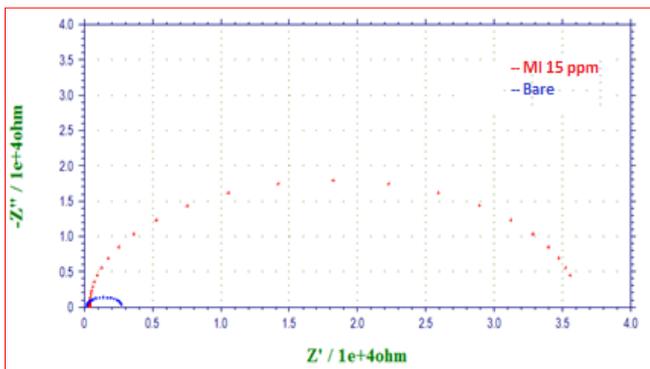


Figure 2. Nyquist plots of bare and SAMs covered copper of conc. 15 ppm in aq. 300 ppm NaCl solution

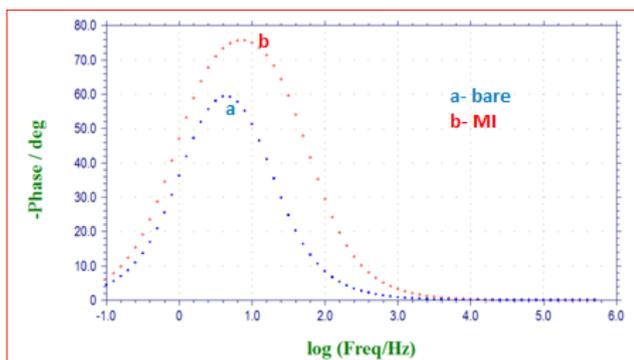


Figure 3. Bode plots of bare and SAMs covered copper in aq. 300 ppm sodium chloride solution

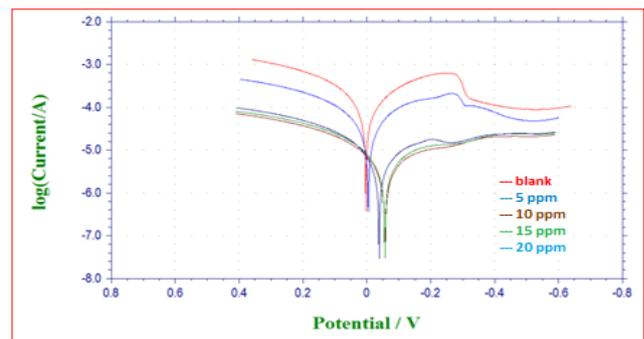


Figure 4. Potentiodynamic polarization curves of bare and SAMs covered copper of conc. 5 to 20 ppm in aq. 300 ppm sodium chloride solution

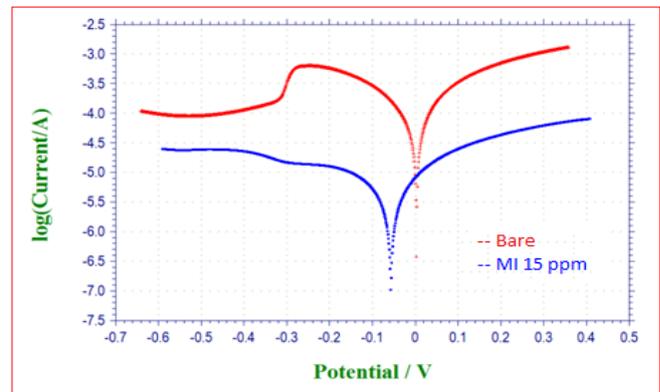


Figure 5. Potentiodynamic polarization curves of bare and SAMs covered copper of conc. 15 ppm in aq. 300 ppm sodium chloride solution

### 3.2.3. Electrochemical Impedance Studies

This is used to characterise the properties of SAMs<sup>12-16</sup>. This study is based on the measurement of the response to an alternating potential of small amplitude. Nyquist plots of bare copper and SAMs covered copper electrodes are obtained in 300 ppm sodium chloride aqueous solution after half an hour equilibration as the open-circuit potentials of the electrodes become steady. Impedance parameters for the bare and SAMs covered copper electrodes are obtained using two different equivalent circuit models<sup>17,18</sup>.

## Self Assembled Monolayers (Sams) of Methimazole on Copper in Corrosion Protection

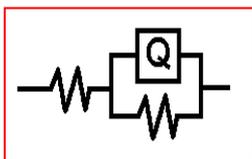


Fig.6.a.

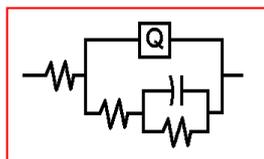


Fig. 6.b

Figures 6.a, b. Equivalent circuits

Bode plots also provide the much needed information than the Niquist plots. The phase angle is found to be the maximum for SAMs covered copper than bare copper which is shown in **figure 3**. The Nquist plots for bare and SAMs covered copper in sodium chloride at different concentrations at a constant immersion period of half an hour, at a temperature of 30<sup>0</sup>C are shown in **figures 1-3**. The impedance data for bare copper and SAMs covered copper are shown in **table 4**. For e.g., The  $R_{ct}$  value for bare copper in 300 ppm sodium chloride solution is 2.56 K $\Omega$  cm<sup>2</sup>, which has increased enormously to 35.75 K $\Omega$  cm<sup>2</sup> for copper covered with SAMs for the same environment. The CPE value at the copper interface is found to decrease from 0.044  $\mu$ F cm<sup>2</sup> to 0.0002  $\mu$ F cm<sup>2</sup> for bare copper to SAMs covered copper. This is because the water molecules in the electrical double layer are replaced to a very large extent by the organic molecules with a very low dielectric constant<sup>19</sup>. The value of n has increased 0.35 to 0.88 from bare copper to SAMs covered copper resulting in the copper surface that has become smoother due to the formation of dense, non-porous monolayer of Methimazole. When the value of n drops to unity slowly, the behaviour of SAMs tends to be an ideal capacitor<sup>16</sup>.

The changes in the double layer capacitance and interfacial capacitance are found to be correlated to SAMs formation. In addition, the polarization resistance, which corresponds to the charge transfer resistance in the pores of the monolayer, is found to increase with the increase of the surface coverage. Since the double layer capacitance is larger than the capacitance of SAMs, it will dominate the total capacitance. The high frequency EIS data is modelled with a Randle's circuit modified with a constant phase element (CPE) in place of the capacitor as shown in **Figure 6**. The impedance of CPE depends on the frequency via the equation,

$$Z_{CPE} = 1/C(j\omega)^n$$

Where, C is capacitance.

The studies of Nahir and Bowden<sup>20</sup> show that electrons can penetrate SAMs even though they are defect free and more-over SAMs are found to contain molecule seized defects<sup>21-24</sup>. Zamborini and Crooks<sup>21</sup> proposed a corrosion reaction model for the electrode covered by SAMs with defects. In this model, the corrosive ions, such as halide ions, can penetrate through SAMs through defects and react with metal substrate, giving rise to the expansion of the defective sites leading to further destruction of SAMs. But hydrocarbons containing nitrogen and sulphur within the SAMs can partially heal the defects.



Hence, in such case, Methimazole {C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>S} containing one sulphur and two nitrogen atoms, bond tightly to the metal surface thus forming a very thick monolayer that prevents the diffusion of corroding chemicals and ions and offers a great protection for copper from corrosion. Inhibition efficiency is calculated using the formula,

$$I.E. = (R_t - R_t^1) \times 100 / R_t$$

where,  $R_t$  the resistance of bare copper and  $R_t^1$  the resistance of SAMs covered copper. The results are found to have a very good correlation with polarization and weight-loss studies.

Thus, all the observations in the impedance studies indicate the formation of non-porous, highly protective film (SAMs) on the metal surface, which effectively protects the metal from corrosion even in aggressive environment like sodium chloride of very lowest concentration where pitting corrosion can be possible. The results are tabulated in **table 7 and 8**.

Inhibitor	$E_{corr}$ (mV)	$I_{corr}$ ( $\mu$ A/cm <sup>2</sup> )	$b_a$ (mV/decade)	$b_c$ (mV/decade)	IE (%)
Bare 1 hr	-101	296	137.02	106.72	-
MI	-20	85.76	195.73	201.45	71
B 2 hr	-125	309.3	139.80	149.39	-
MI	-21	85.07	195.08	200.40	69
B 4 hr	-127	505.7	169.09	141.14	-
MI	-21	82.25	194.28	200.20	84
B 6 hr	-138	508.5	148.87	167.70	-
MI	-21	81.17	194.59	198.49	82

Table 5. Corrosion parameters obtained from potentiodynamic polarization studies of bare and SAMs covered copper at different immersion periods in aq. 300 ppm chloride

Conc. (ppm)	$R_{ct}$ ( $K\Omega\text{ cm}^2$ )	Cdl ( $\mu\text{F cm}^2$ )	n	IE (%)
Bare 1 hr	1.36	0.166	0.25	-
MI	5.744	0.0093	0.64	76
B 2 hr	0.222	6.261	0.15	-
MI	3.227	0.0291	0.90	93
B 4 hr	0.198	7.804	0.15	-
MI	5.173	0.0112	0.94	96
B 6 hr	0.154	12.867	0.12	-
MI	3.981	0.0195	0.94	96

Table 6. Impedance parameters of bare and SAMs covered copper at different immersion periods in aq. 300 ppm chloride

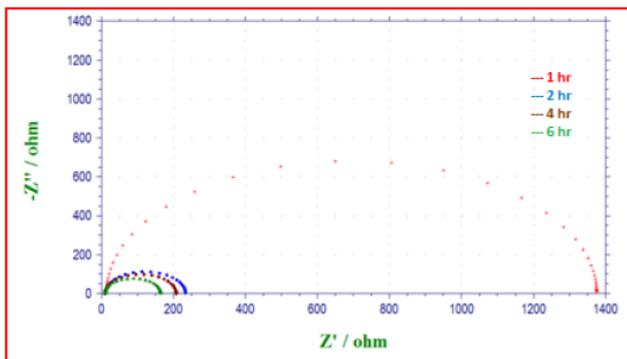


Figure 7.a. Nyquist plots of bare copper at different immersion periods in aq. 300 ppm chloride

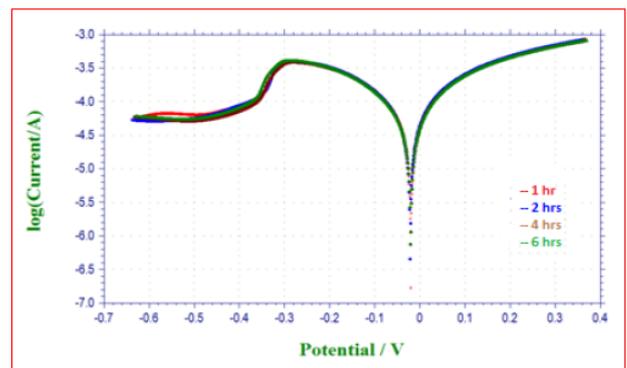


Figure 8.b. Potentiodynamic polarization curves of 15 ppm inhibitor solution at different immersion periods in aq. 300 ppm chloride

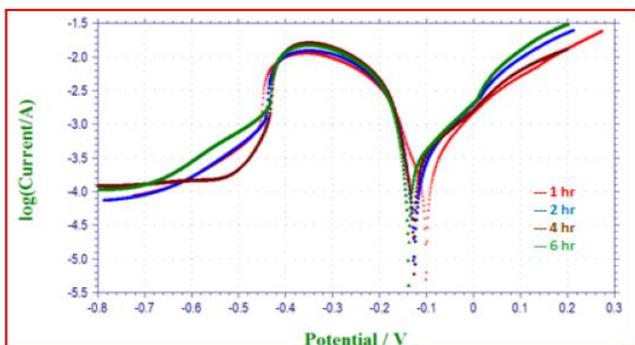


Figure 7.b. Potentiodynamic polarization curves of bare copper at different immersion periods in aq. 300 ppm chloride

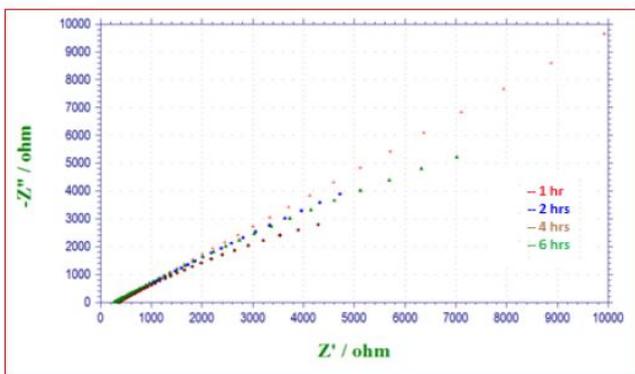


Figure 8.a. Nyquist plots of 15 ppm inhibitor solution at different immersion periods in aq. 300 ppm chloride

Inhibitor	$E_{cor}$ (mv)	$I_{corr}$ ( $\mu\text{A/cm}^2$ )	$b_a$ (mV/decade)	$b_c$ (mV/decade)	IE (%)
Bare 100 ppm	-94	418.2	187.30	171.43	-
MI	-3	36.77	192.52	245.94	91
B 150ppm	-	502.5	186.15	175.44	-
MI	-6	39.47	193.53	230.41	92
B 200ppm	-	491.5	173.34	161.84	-
MI	-3	69.82	194.48	202.39	86
B 250 ppm	-	183.3	175.31	158.77	-
MI	-4	82.58	191.35	201.41	55
B 300 ppm	+3	125.4	192.38	189.86	-
MI	-56	6.36	182.98	281.61	95

Table 7. Corrosion parameters obtained from potentiodynamic polarization studies of bare and SAMs covered copper of 15 ppm inhibitor concentration in different concentrations of aq. Sodium chloride solution.

Conc. (ppm)	$R_{ct}$ ( $K\Omega$ $cm^2$ )	Cdl ( $\mu F$ $cm^2$ )	n	I.E.(%)
Bare 100	0.843	0.4183	0.2	-
MI	7.131	0.00609	0.85	88
B 150	0.728	0.5496	0.19	-
MI	3.659	0.0220	0.77	80
B 200	0.680	0.6423	0.18	-
MI	3.767	0.0217	0.78	82
B 250	0.375	2.050	0.16	-
MI	3.387	0.0269	0.86	89
B 300	2.56	0.044	0.35	-
MI	35.75	0.0002	0.88	93

Table 8. Impedance parameters of bare and SAMs covered copper of 15 ppm inhibitor concentration in different concentration of aq. Sodium chloride solution

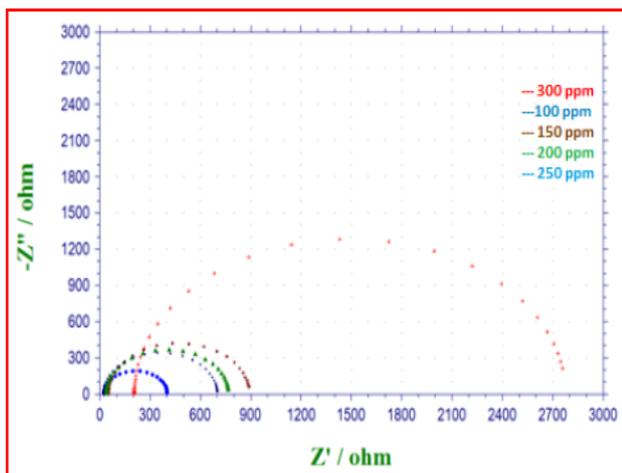


Figure 9.a. Nyquist plots of bare copper in different concentrations of aq. Sodium chloride solution

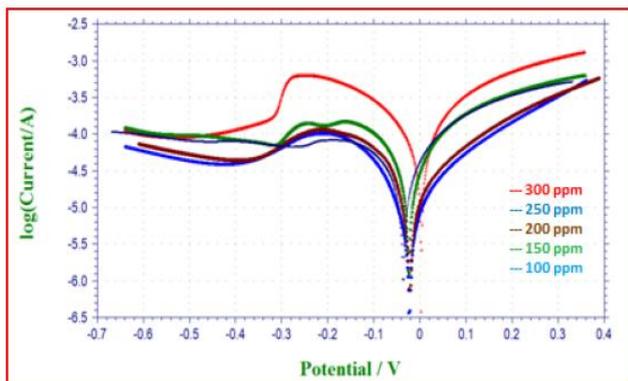


Figure 9.b. Potentiodynamic polarization curves of bare copper in different concentrations of aq. Sodium chloride solution

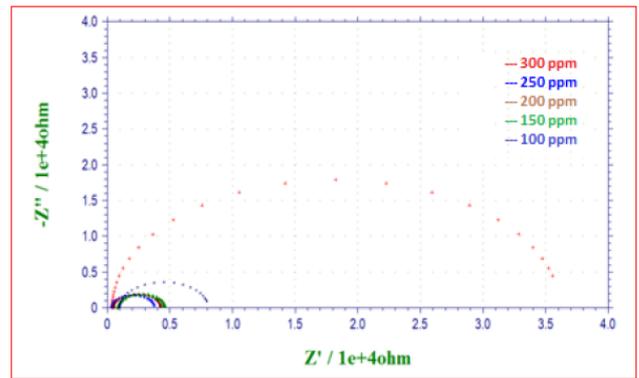


Figure 10.a. Nyquist plots of 15 ppm inhibitor solution in different concentrations of aq. Sodium chloride solution

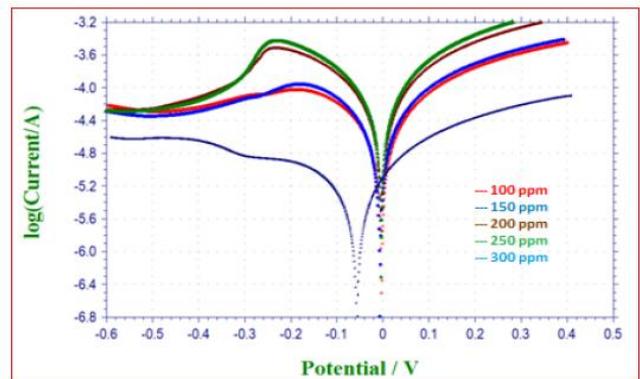


Figure 10.b. Potentiodynamic polarization curves of 15 ppm inhibitor solution in different concentrations of aq. Sodium chloride solution These results are also in good agreement with the results obtained in the literature for different SAMs on copper<sup>25-26</sup>.

### 3.2.4. CV studies

The cyclic voltammograms of bare and SAMs covered copper for 2 cycles at a sweep rate of 100 mV/s are shown below. For bare copper, there exists two oxidation peaks at 0.140 V and 0.180 V in the forward scan, first due to the formation of CuCl and the second due to the formation of soluble  $CuCl_2^-$  complex and a large reduction peak at -430 V in the reverse scan, which is due to the reduction of  $CuCl_2^-$ . The SAMs covered copper exhibits no oxidation peak and one reduction peak at -0.16 V in the reverse scan, which has very slight change to -0.2 V after 15 cycles. Compared to bare copper, the anodic and cathodic peak currents of SAMs covered copper has decreased to the maximum from  $4 \times 10^{-3}$  A to  $2.6 \times 10^{-4}$  A for anodic and from  $-4.8 \times 10^{-3}$  A to  $-0.5 \times 10^{-4}$  A, which has a very slight change to  $-1 \times 10^{-4}$  A even after 15cycles, which is not very significant and the oxidation of Cu(0) to Cu(I) has inhibited strongly due to the formation of imidazole film on the surface. These results infer the stability of imidazole film on the copper surface, which provides the evidence for the protection of copper in corrosive sodium chloride environment.

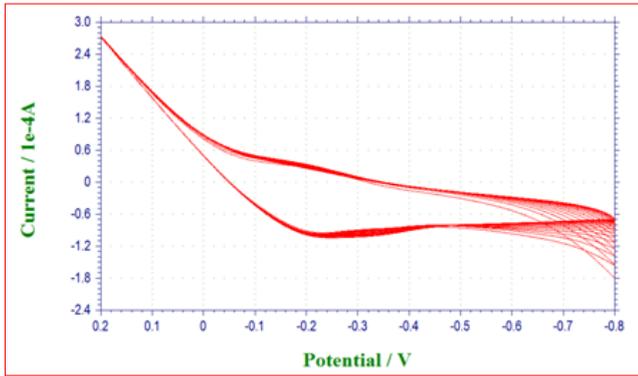


Figure 11. CV for bare copper in aq. 300 ppm NaCl at a sweep rate of 100 mV/s

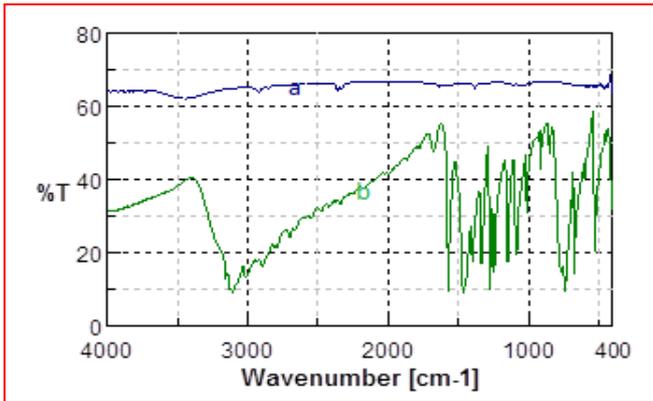


Figure 12.a. Cyclic voltammogram of SAMs covered copper in aq. 300 ppm sodium chloride solution at a sweep rate of 100mV/s for 15 cycles

### 3.3. SURFACE CHARACTERISATION STUDIES

#### 3.3.1. IR Studies

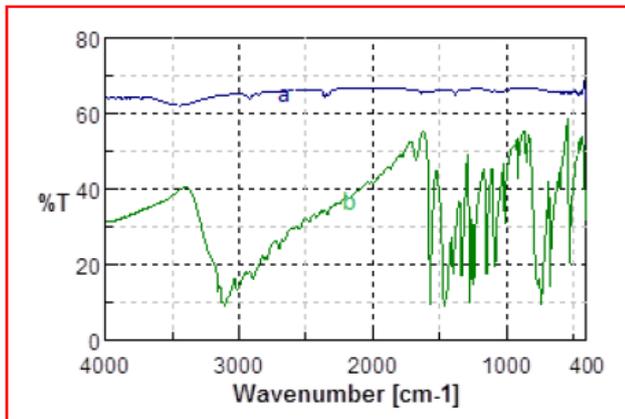


Figure 13. FT-IR spectra of a) SAMs covered copper and b) pure imidazole

FT-IR spectra for bare and SAM covered copper are shown below. They show the appearance of peaks at 1243  $\text{cm}^{-1}$ , 2922  $\text{cm}^{-1}$ , which correspond to C - N and C-H asymmetric stretching respectively.<sup>17,25</sup> These peaks infer the presence of SAMs of Methimazole on copper surface. The lowering of C - N stretching from 1276 to 1243  $\text{cm}^{-1}$ <sup>26</sup> refers to the formation of complex between SAMs and copper surface through Nitrogen atom. These identified peaks are found to be similar with the peaks of pure inhibitor compound which appear at 1273  $\text{cm}^{-1}$ , 2938  $\text{cm}^{-1}$ . The peak at 505  $\text{cm}^{-1}$  might be due to the adsorption of

oxygen on copper surface during the formation of SAMs. For bare copper, there appeared two peaks at 445  $\text{cm}^{-1}$  and at 489.5  $\text{cm}^{-1}$ , which are assigned to cuprous oxide formed on the surface of the copper metal (Yoshida and Ishida, 1995). Thus, the shift towards lower frequency range shows the adsorption of nitrogen, which prevents the attack of corrosive elements mainly like oxygen, and shows a very clear evidence for the presence of aliphatic hydrocarbon chain through SAMs formation. Whereas, for bare and corroded copper, the IR frequency range shifts towards the high frequency range, which proves that the copper metal gets corroded without the presence of nitrogen and sulphur which lead to the formation of SAMs and offer a very high inhibiting efficiency.

#### 3.3.2. SEM studies

SEM studies of polished bare and SAMs covered copper are studied in 300 ppm of neutral medium for three days. The SAMs covered copper plate after an immersion of 24 hrs in the inhibitor solution in ethanol is immersed in 300 ppm sodium chloride solution for three days and pictures of SEM analysis in Fig.14.a. & b. show that most of the area of the bare copper has been corroded due to the adsorption of chloride ions and the surface appears very rough due to the uneven formation of the corrosion products. In Fig 14.a, the SAMs coated copper plate has a smooth uniform coverage of Methimazole molecule of 15 ppm concentration, without any defective site and thus prevent the adsorption of chloride ions and resist corrosion with a very high inhibition efficiency. The figures of the SAMs covered copper plates differ from pure polished surface (with some defective sites) by forming a smooth uniform monolayer throughout.

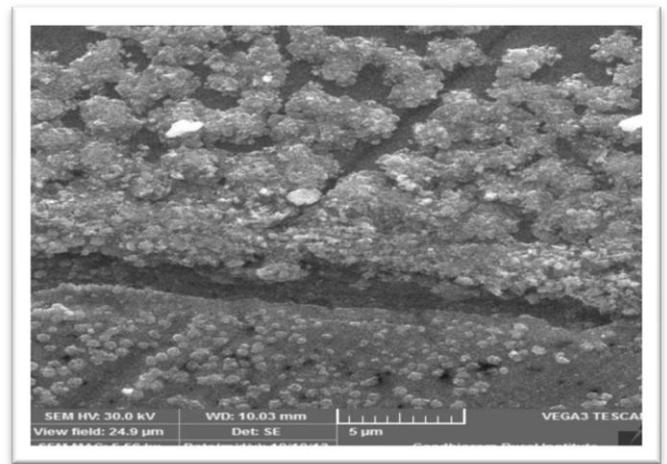


Figure 14. SEM image of copper in 300 ppm NaCl

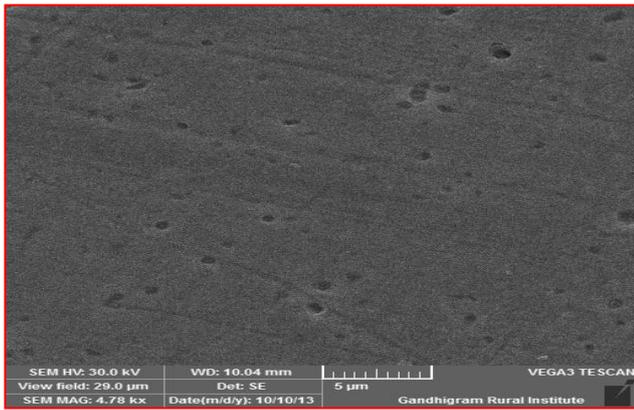


Figure 15. SEM image of pure polished copper

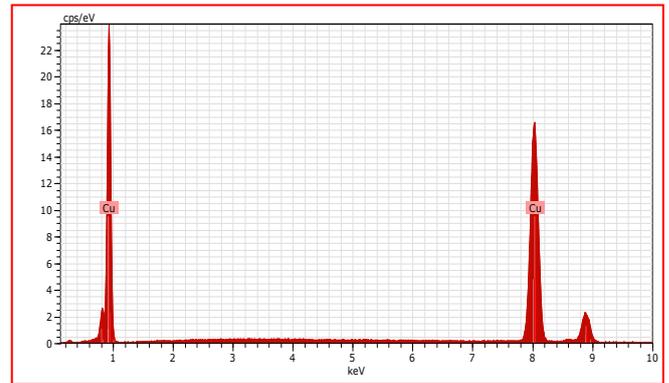


Figure 17.b. EDX analysis of pure copper

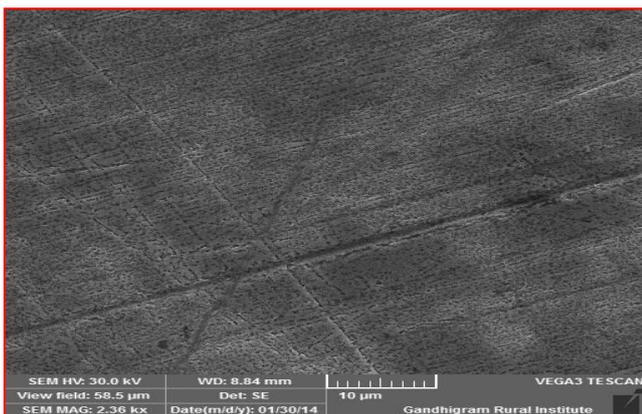


Figure 16 SEM images of SAMs covered copper in 300 ppm NaCl

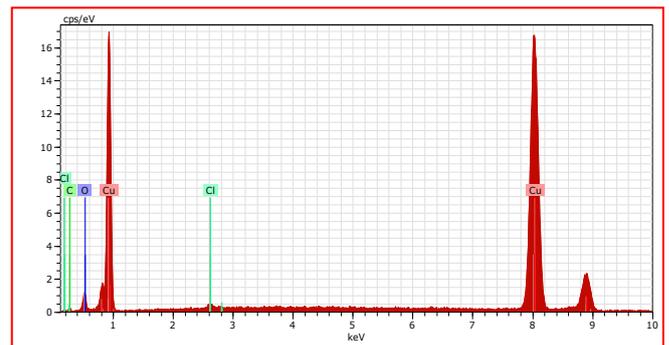


Figure 17.c. EDX analysis of pure copper in 300 ppm NaCl

### 3.3.3. EDX studies

The figures 17.a, b, c, show the surface morphology for the elemental identification of bare and SAMs covered copper in aqueous 300 ppm sodium chloride solution and of pure copper had been studied through EDX studies and it clearly shows the presence of chloride in bare copper specimen and the adsorption of nitrogen, sulphur, in SAMs coated copper specimen, which cover the whole surface forming a uniform protective layer and the absence of corroding elements like chlorine and oxygen prove the dense formation of monolayer that offers a very higher inhibition efficiency and prevents the diffusion of corroding elements and isolated copper from corroding environment.

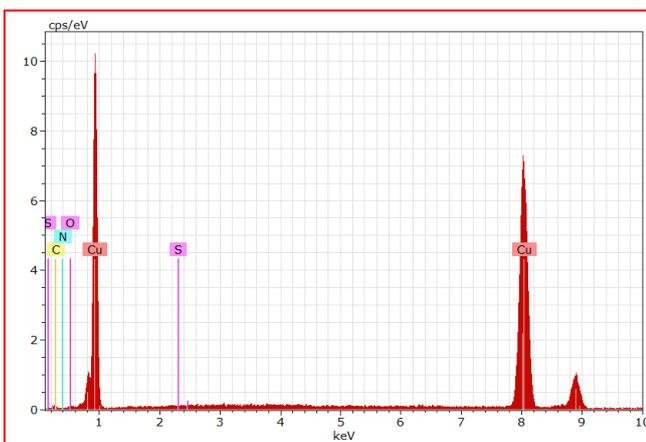


Figure 17.a. EDX analysis of SAMs covered copper in 300 ppm NaCl

### 3.3.4. Contact angle measurements

Fig. 18.a. and b. show the images of sessile water drop on SAMs covered copper and bare copper surfaces respectively, which prove the hydrophobicity of SAMs covered copper due to the strong adsorption of nitrogen and sulphur on the copper substrate over bare copper by preventing the diffusion of corroding ions in protecting the copper substrate from corrosion. The contact angles are found to be  $108.4^{\circ}$  and  $76.0^{\circ}$  respectively for SAMs covered and bare copper, in which the non-polar interaction between the alkyl chains of the molecules due to van der waals' forces are responsible for protective quality of the SAMs film. The hydrophobicity of the film formed is found to be equal with the hydrophobic film of Amino thiol which offers a very high inhibition efficiency.

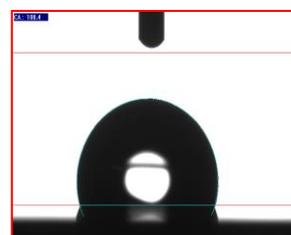


Fig.18.a.

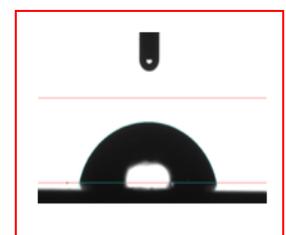


Fig. 18. b.

Figures 18. a. & b. Contact angle images of SAMs covered and bare copper

3.3.5. AFM studies

The topography of the surfaces recorded in 2D and 3D images is examined and surface roughness, root-mean-square roughness (Rms), mean roughness factor (Ra) are determined from the respective images. **Table 9** shows various AFM parameters obtained for SAMs covered copper surface. **Figures 21.a, b, c, d** show the AFM images and cross section analysis of SAMs covered copper surface, with an Ra value of 0.9504 $\mu\text{m}$ , Rms value 1.404  $\mu\text{m}$  indicates the absence of SAMs. A severely corroded surface morphology (**Figures 20.a, b, c,**) is observed after immersion in 300 ppm aqueous sodium chloride solution, with an increased Ra value 2.435  $\mu\text{m}$ , Rms value 2.463  $\mu\text{m}$  indicate the adsorption of chloride ions and the formation of corrosion products. The root-mean-square (RMS) roughness is found to be 2.463  $\mu\text{m}$ , which clearly indicates the roughness of the corroded surface. The microstructure of the surface shows several smaller and larger corrosion product deposits. Whereas, decrease in roughness of the SAMs covered copper surface shows the dense, uniform adsorption of imidazole on the metal.

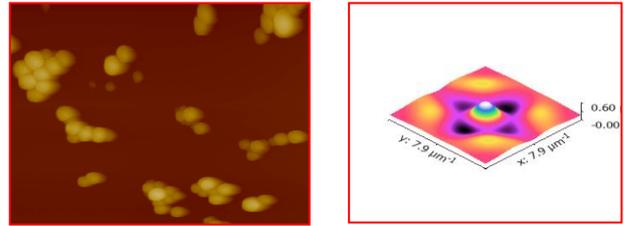


Fig. 20.a. 2 D image of bare copper

Fig. 20.b. 3D image of bare copper

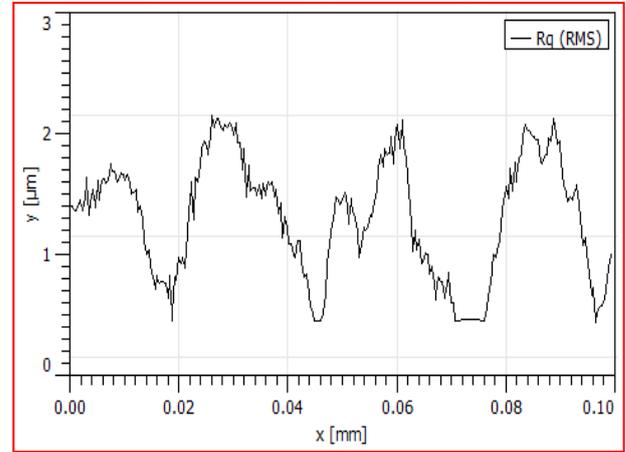


Figure 20.c. RMS measurements

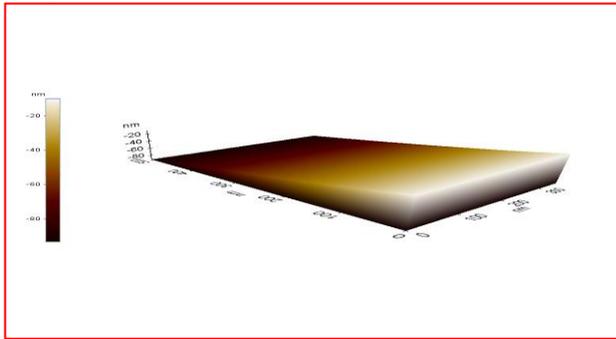


Fig. 19.a. 2 D image of polished copper

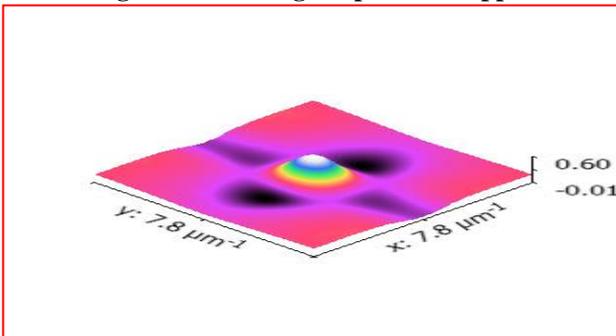


Fig. 19.b. 3 D image of polished copper

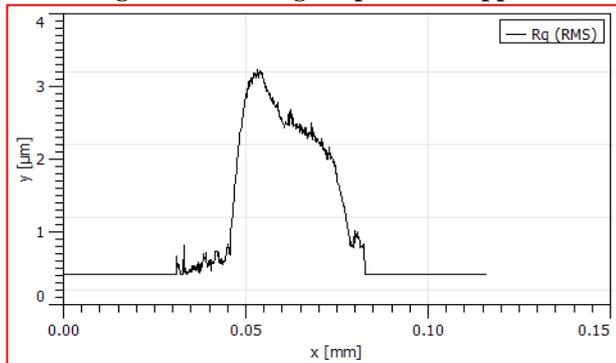


Fig. 19.c. RMS measurements

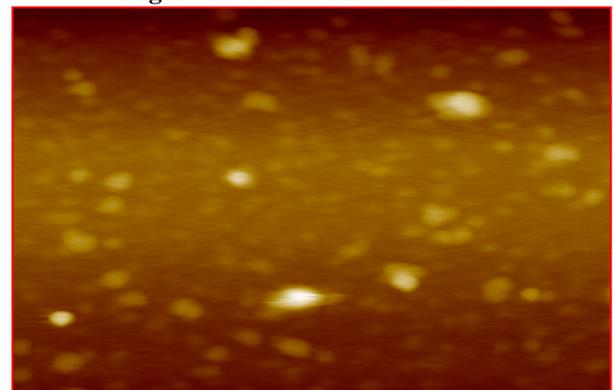


Figure 21.a. 2 D image of SAMs covered copper

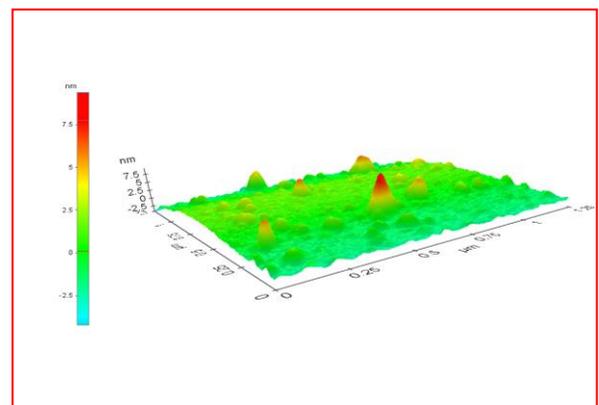


Figure 21.b. 3 D image of SAMs covered copper

## Self Assembled Monolayers (Sams) of Methimazole on Copper in Corrosion Protection

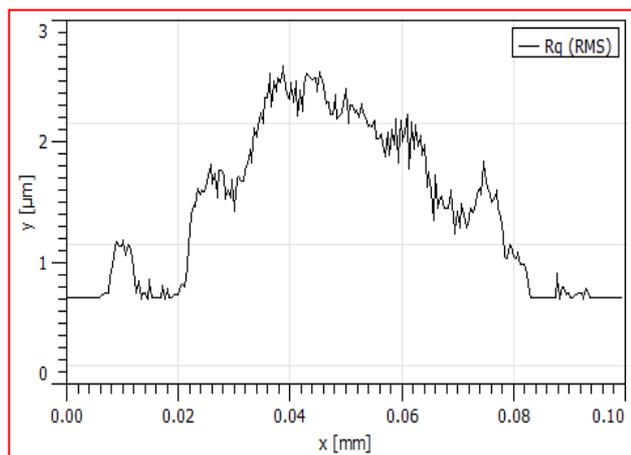


Figure. 21.c. RMS measurements

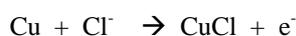
Environment	Ra ( $\mu\text{m}$ )	Rms ( $\mu\text{m}$ )
Polished Cu metal	0.9504	1.404
Polished Cu metal in 300 ppm Cl-	2.435	2.463
SAMs covered metal surface	<b>1.219</b>	<b>1.744</b>

Table 9. AFM parameters

The decrease in RMS roughness from 2.463 $\mu\text{m}$  for bare to 1.744  $\mu\text{m}$  for SAMs covered copper clearly infers the greater smoothness and homogeneity of the surface film produced by the inhibitor and the absence of any corrosion product deposits, which offer a protective layer thereby, forming a barrier against the attack of aggressive ions from the corrosive environment.

### 3.3.7. MECHANISM

It is known that the corrosion process of copper in aerated sodium chloride solution comprises anodic dissolution of copper and cathodic reduction of oxygen<sup>27-29</sup>. The anodic dissolution of copper is shown as



and cathodic reduction of oxygen is given by,



The mechanism involves the formation of a non-porous, dense, protective film on copper surface. Relatively higher contact angle value (108.4<sup>0</sup>) of imidazole film than bare copper of 76.0<sup>0</sup> reveals the hydrophobic nature, which is due to the orientation of alkyl chain. All these results indicate the formation of a dense and defect free film on copper surface, which is highly protective in nature.

## IV. CONCLUSION

It is concluded that under these optimum conditions, i) polishing to mirror finish using 1-6 emery grade sheets, ii) degreasing with acetone, iii) ethanol solvent, iv) 10 ppm imidazole solution, v) 24 hour immersion, the formation of self-assembled monolayers on copper surface occur

using Methimazole and it offers excellent corrosion protection to copper in sodium chloride environment. SAMs molecules get chemisorbed on the copper metal surface and form co-ordination complex with Cu (II) ions through nitrogen atom. The inhibition efficiencies obtained from Polarization, Impedance and Weight-loss studies, offer a very good correlation with each other and the results of SAMs CV results prove the stability of SAMs. It is confirmed that the protective monolayer formed on the copper surface plays a very vital role in corrosion inhibition of copper.

## REFERENCES

- H. Kondoh, N. Saito, F. Matsui, T. Yokoyama, T. Ohta, H. Kuroda, J. Phy. Chem. Soc. B 105 (2001) 12870.
- S. Pathak, A.S. Khanna, Indian Journal of Chem. Tech., Vol.14 Jan.2007 pp. 5-15.
- Ulman. Chem Rev. 96 (1996) 1533.
- P. E. Laibins & Whitesides J Am Chem Soc, 117(1995) 12009.
- R G Nuzzo & D C Allara, J Am Chem Soc, 105 (1983) 4481.
- Z. Qian, X. Wu, S. Chen, S. Zhao, H. Ma, Corrosion 57 (2001) 195.
- Miki Ishibashi, Miki IToh, Kiroshi Nishihara, Kunmitsugu Aramaki, Electrochim. Acta 41 (1996) 241.
- M. Yadav, D. P. Sharma, Indian Journal of Chem, Tech., Vol.17 March 2020, pp 95-101.
- El-sayed M. Sherif, Int, J. Electrochem. Sci., 7 (2012) 1884-1887.
- B.V. Apparao, Md.Iqbal, B.Sreedhar, Indian Journal of Chem. Tech., Vol.16 Jan.2009 pp.25-31.
- B. Brzoska, N. Shahidzadeh. F. Rondelez, Nature 360 (1992) 719.
- O. E. Barcia, O. R. Mattos, N. Pebere, B. Tribollet, J. Electrochem. Soc. 140 (1993) 2825.
- Y. Feng, W. K. Teo, K. S. Siow, K. L. Tan, A. K. Heish, Corros. Sci. 38 (1996) 369.
- X. Wu, H. Ma, S. Chen, Z. Xu, A. Sui, J. Electrochem. Soc. 146 (1999) 1847.
- C.T. Wang, S. H. Chen, h. Y. Ma, L. Hua, N. X. Wang, J. Serb. Chem. Soc. 67 (10) (2002) 685.
- H. Y. Ma, C. Yang, S. H. Chen, Y. L. Jiao, S. X. Huang, D. G. Li, J. L. Luo, Electrochim. Acta 48 (2003) 4277.
- V. Appa Rao, Md. Yakub Iqbal, B. Sreedhar, Corrosion Science 51 (2009) 1441-1452.
- Guiyan Li, Houyi Ma, Yongli Jiao, Shenhao Chen, J. Serb. Chem. Soc. 69 (10) (2004) 791.
- C.T. Wang, S. H. Chen, h. Y. Ma, L. Hua, N. X. Wang, J. Serb. Chem. Soc. 67 (10) (2002) 685.
- T. M. Nahir, E. F. Bowden, Electrochim Acta 39 (1994) 2347.
- F. P. Zamborini, R. M. Crooks, Langmuir 14 (1998) 3279.
- Sun, R. M. Crooks, Langmuir 9 (1993) 1951.
- O. Chailapakel, L.Sun, C. Xu, R. M. Crooks, J. Am. Chem. Soc. 115 (1993) 12459.
- X. M. Zhao, J. L. Wilbur, G. M. Whitesides, Langmuir 12 (1996) 3257.
- Lalitha. S. Ramesh, S. Rajeswari, Electrochim Acta 51 (2005) 47.
- H. Baba, T. Kodama, K. Mori, H. Hirahara, Corros. Sci. 39 (1997) 555.
- Chun-Tao Wang, Shen-Hao Chen, Hou-Yi Ma, Ian Hua & Nai-Xing Wang, J. Serb. Chem. Soc. 67 (10) 685-696 (2002).
- H. P. Lee, K. Nobe, J. Electrochem.Soc. 133 (1986) 2035.
- Deslouis, B. Tribollet, G. Mengoli, M. M. Musiani, J. Appl. Electrochem. 18 (1988) 374.