Formation, investigation and characterization of self-assembled monolayers of 5-methyl-1,3,4-thiadiazole-2-thiol in corrosion protection of copper in neutral media

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ABSTRACT

Self assembled monolayer is formed on copper using 5-Methyl -1,3,4-thiadiazole, 2-thiol, under optimum conditions. Corrosion behaviour of copper is studied in neutral medium of 300ppm using Gravitmetry, electrochemical (impedance, potentiodynamic polarization)studies, FT-IR, SEM, EDX, XPS and AFM studies, using 5-Methyl - 1,3,4-thiadiazole,2-thiol. Using gravimetric studies, an efficiency of 100% is obtained. Electrochemical impedance studies with high charge transfer resistance values reveal that self-assembled thiol monolayers formed offer a very high inhibition efiiciency. Potentiodynamic polarization studies have shown that SAMs formation controls both anodic and cathodic reactions. Scanning electron microscopic studies have revealed the chemisorption of nitrogen and sulphur on the metal surface. CV studies have proved the stability of SAMs and the thickness of SAMs formed can be proved through AFM studies. Thus SAMs formed using thiol offer a very good inhibition efficiency in protecting copper against corrosion.

Keywords: Corrosion inhibition, SAMs, 5-Methyl-1,3,4-thiadiazole-2-thiol.
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INTRODUCTION

The corrosion of copper and other metals occur usually when it is exposed to air. Copper is also exclusively used for piping and delivery of water for marine industries, which mainly contain 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 through modifying its surface by forming self- assembled densely oriented monolayers using suitable organic inhibitors that contain mainly nitrogen and sulphur atoms which can adher easily to the metal surface. The strong chemical interaction between sulphur atoms and the metallic surface leads to the formation of chemisorbed organic films. SAMs include simplicity of preparation, stability and the possibility of introducing different chemical functionalities [1-3]. Several different varieties of SAMs have been investigated including alkanethiols ($CH_3(CH_2)_{n-1}SH$) on Au, Ag and Cu and alkyltrichlorosilanes ($CH_3(CH_2)_{n-1}SiCl_3$) on SiO_2, Al_2O_3 and mica[4,5]. The chemisorptions of alkanethiol with long hydrocarbon chains provides densely packed SAMs on the surface. SAMs on copper surfaces have been found to be effective inhibitors for copper corrosion[6]. Kondoh et al have investigated alkanethiolate monolayers on Cu(100) and found that sulphur atom in the thiolate occupies the 4-fold hollow site of the unreconstructed Cu(100) surface[7]. In case of alkanethiols on a

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Au(111) surface, they are strongly chemisorbed on the gold surface by the formation of a covalent-like bond between gold and sulphur atoms following cleavage of a sulphur-hydrogen bond. Although the copper surfaces differ in structural details from the Au(111) surface, it has been concluded that the structures of SAMs on copper are qualitatively similar to those on gold[8].

Self-assembled monolayers(SAMs) offer a simple method to get a monomolecular film in nanometer range. SAMs formation needed a very small quantity of organic corrosion inhibitor, which is economically very attractive and eco-friendly. SAMs of organosulphur compounds are expected to function as a barrier to prevent the permeation of corrosion accelerants such as moisture and electrolyted into the copper substrate, thereby improving the corrosion resistance of copper[9-12]. It improves the interaction between first monolayer of inhibitor and copper by chemisorption. It has therefore become an interesting pretreatment of surface before applying of organic coating[13]. Widespread examples were alkanethiol monolayer[14-20], silane[21,22]/alkylisocyante[23] modified alkanethiol monolayer, Schiff base monolayer[24,25] and N-Vinylcarbazole monolayer[26] on oxide free copper.

The aim of present study is to investigate the ability of SAMs of 5-Methyl-1,3,4-thiadiazole-2-thiol on copper surface in sodium chloride environment using Wt.loss, impedance, potentiodynamic, SEM and EDX ,Water contact angle measurements, AFM and XPS studies for the confirmation of adsorption of nitrogen and sulphur atoms on the metal surface in forming self-assembled monolayers.

MATERIALS AND METHODS

It is the same as discussed in, "Self-assembled monolayers (SAMs) of Methimazole on copper in corrosion protection" (Rajalakshmi Devi et al/ IJRTE/ Vol 4/ Issue 2/ May 2015)

RESULTS AND DISCUSSION

As discussed earlier, the formation of Self-Assembled Monolayers on the metal substrate follows a two step process, i.e., the fast adsorption step and the second one the rearrangement step. The self-assembled monolayers aggregate themselves by Vander Waals' force and the head group attaches with the metal substrate by the cleavage of the S-H bond. To obtain uniform, densely packed SAMs, the metal substrate is pre-treated, using HNO_3 for few seconds, then polished to mirror finish using different grade emery sheets and degreased with acetone at room temperature. As already discussed in section 2, ethanol is chosen as the solvent with an immersion time of 24 hr. The optimum concentration of thiol and immersion period are also established through impedance studies.

3.1. Effect of concentration of thiol film
As reported in the literature, a well ordered dense SAMs can be formed with an immersion period more than 20 hrs. The results of the present study shows that an immersion period of 24 hrs have enhanced the formation of the protective film. Hence an immersion period of 24 hrs have been chosen initially and thiol films are formed on the copper substrate at various concentrations of 5-methyl-1,3,4-thiadiazole-2-thiol from 5 ppm to 20 ppm. Impedance studies have been carried out in aq. 300 ppm sodium chloride solution after an equilibration of half an hour for the open circuit potentials to become steady and the 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 5 ppm thiol is found to be the maximum and it decreases with further increase in concentration. Hence, thiol of 5 ppm concentration is chosen as the optimum concentration to form SAMs, which shows a maximum inhibition efficiency thereby protecting the metal surface by preventing the diffusion of chloride ions from the solution and the diffusion of Cu^+ ions from the metal surface to the solution. The impedance parameters are shown in **table 4**.The charge transfer resistance value have been found to the maximum as 55.19KΩ cm^2, with the much decrease in C_{dl} value of 0.000098 μF cm^2 and the constant exponent 'n' value of 0.94, reveals the dense protective film formation on the copper substrate.

3.1.1. Effect of immersion period
Within the errors of experiment and theoretical treatment, this value approaches the capacitance values obtained by fitting impedance spectra in the immersion times from 1 to 6 hrs in NaCl solution, thereby proving that the equivalent circuits for the SAMs coated electrode are creditable and the analysis and treatment for impedance data are reasonable. The corrosion mechanism of the copper electrode modified by SAMs in 300 ppm sodium chloride solution can be interpreted by the reaction models shown in **figures 6** below. In sodium chloride solution, the electrochemical corrosion of copper substrate can occur when both oxygen molecules and chloride ions reach the

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bare copper surface[27] through the defects within SAMs. Because the oxygen concentration in the sodium chloride solution is low and 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 thiol SAMs is relatively stable and can strongly protect the copper substrate from corrosion in sodium chloride solution. The increase in R_{ct} value from 4 to 6 hrs immersion is considerably less, hence the SAMs formed is found to be stable within 6 hrs which is shown in **figure 8.a.**

3.2. Corrosion protection of SAMs film
3.2.1. **Weight loss Studies**
The inhibition efficiency of the corrosion rates have been expressed in $mg/dm^2/day$. The specimens are weighed before immersing it in the inhibitor solution and after the formation of SAMs on the specimens, i.e, after a period of 24 hrs immersion, the specimens are taken out, rinsed with ethanol solution, dried and weighed. These weighed samples after SAMs formation 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 sodium chloride solution have been calculated using I.E. = ($\Delta W - \Delta W_1$) × 100 /ΔW, Where ΔW and ΔW_1 are the decrease in weights of bare copper plate and SAMs covered copper plates respectively. 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.** And the SAMs covered copper is found to have an efficiency of 100.% from the datas shown in the table below.

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

S. No	Concentration (ppm)	C.Rate (mg/dm²/day)	IE (%)
1.	5	0.0000	100
2.	10	0.2447	99
3.	15	1.9811	89
4.	20	0.7418	96
5.	25	1.245	93
6.	30	0.9876	95

Table 2. Corrosion rates from weight loss studies for a period of 10 days immersion.

S.No.	Conc. (ppm)	C.Rate (mg/dm²/day)	IE (%)
1.	5	0.5247	97
2.	10	0.7474	96
3.	15	0.6065	97
4.	20	1.607	91
5.	25	0.9029	95
6.	30	0.2991	98

Corrosion rate is calculated using the formula below:

$$\frac{Loss\,in\,wt.(mg)}{Surface\,area\,of\,specimen(dm2) \times period\,of\,imm.(days)}$$

Whereas the surface area in turn is calculated using,

SA (dm2) = 2 [(L x B + B x T + L x 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.

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 5-methyl-1,3,4-thiadiazole-2-thiol, 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[28]**. The corrosion current densities (I_{corr}) have been determined from the

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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. On comparing with bare copper in sodium chloride solutions, lower I_{corr} values are obtained for SAMs covered copper in sodium chloride solution for all concentrations. The results are shown in **table 8**. The corrosion inhibition efficiency of SAMs covered copper is found to be 94%. These results are in good agreement with impedance studies and find good correlation with the results obtained from weight loss studies. The corrosion potential(E_{corr})for SAMs covered copper shift more towards negative side. The corrosion potential for SAMs covered copper is found to be much lower than bare copper, which is shifted more to cathodic side, while the shift in anodic slope is very less. The inhibition efficiencies of SAMs covered copper are in the range of 94- 99 % 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 -25 mv, which is shifted more to cathodic side. The corrosion current densities for bare copper and SAMs covered copper in 300 ppm sodium chloride solution is found to be 125.4 µA and 73.89 µA respectively. The anodic and cathodic tafel slopes for bare in 300 ppm sodium chloride solution is found to be 192.38 mV/decade and 189.86 mV/decade respectively. And for SAMs covered copper, it is found to be191.24 mV/decade and 856.16 mV/decade respectively. This shows that SAMs controls both anodic and cathodic reactions, but cathodic reaction to a larger extent. The anodic reaction is given by the dissolution of copper into $CuCl$ and $CuCl_2^-$ and the dissolution is determined by the rate of diffusion of soluble $CuCl_2^-$ species[29]. The presence of sulphur and nitrogen in the metal surface in SAMs suppress the formation of $CuCl$ or in other words the diffusion of $CuCl_2^-$ 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, inhibited copper from getting corroded. Thus, the SAMs formation offer a very high inhibition efficiency of 99 % and protect copper from pitting corrosion also. And the inhibition efficiency have been calculated using the formula,

I.E (%) = (i_{corr}-i^1_{corr}) × 100 / i_{corr} ,

Where i_{corr} and i^1_{corr} are the corrosion current densities of bare copper specimen and SAMs covered copper specimen respectively and the inhibition efficiency is found to be 94% as said earlier above.

Table 3. Impedance parameters of bare and SAMs covered copper in aq. 300 ppm sodium chloride solution at different inhibitor concentrations

Conc. (ppm)	R_{ct} (KΩ cm^2)	Cdl(µFcm^2)	n	IE (%)
Bare copper	2.56	0.044	0.35	-
5	**55.192**	**0.000098**	**0.92**	**95**
10	7.754	0.0034	0.56	67
15	13.576	0.0016	0.76	81
20	12.841	0.0018	0.75	80

Table 4. Corrosion parameters obtained by potentiodynamic polarization studies of bare and SAMs covered copper in aq. 300 ppm NaCl solution at different inhibitor concentrations

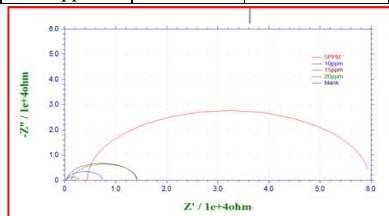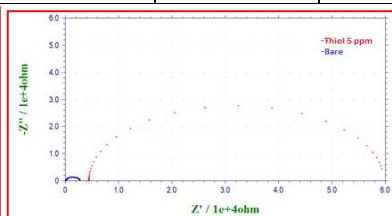| Inhibitor	E_{corr} (mv)	I_{corr} (µA/cm^2)	b_a (mv/decade)	b_c (mv/decade)	IE (%)
Bare copper	+3mv	125.4	192.38	189.86	-
Thiol 5 ppm	**-25mv**	**73.89**	**191.24**	**856.16**	**94**
10 ppm	-26mv	17.60	794.74	2100.84	86
15 ppm	-19mv	3.465	178.47	321.84	97
20 ppm	-2mv	6.493	180.54	212.13	96

| **Figure 1.** | **Figure 2.** |

. Niquist plots of bare and SAMs covered copper in aq. 300 ppm sodium chloride solution
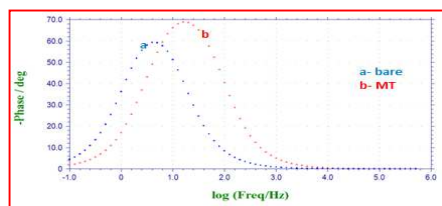**Fig. 1) of conc. 5 to 20 ppm Fig. 2) of conc. 5 ppm**

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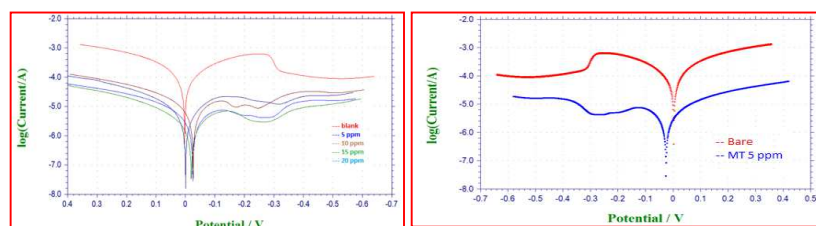

Figure 4	Figure 5

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

3.2.3. Electrochemical Impedance Studies

This is used to characterise the properties of SAMs[30-34]. This study is based on the measurement of the response to an alternating potential of small amplitude. Nquist plots of bare copper and SAMs covered copper electrodes are obtained in 300 ppm aqueous sodium chloride solution after ½ 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 three different equivalent circuit models[35,36].
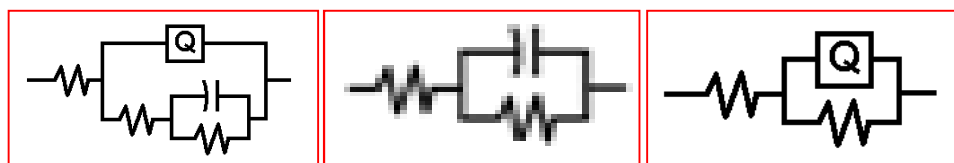
Fig. 6.a.	Fig. 6.b.	Fig. 6.c.

Figure 6.a., b. & c. Equivalent circuits

Bode plots also provide the much needed information than the Niquist plots. The phase angle is maximum at 70^0 for SAMs covered copper than for bare copper. The Nquist plots for bare and SAMs covered copper in sodium chloride at different concentrations at a constant immersion period of ½ an hr, at a temperature of 30^0C 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 2.56KΩ cm^2, which have increased enormously to 55.192 KΩ cm^2 for copper covered with SAMs for the same environment. The CPE value at the copper interface is found to decrease from 0.044 µFcm^2 to 0.000098 µFcm^2 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 having a very low dielectric constant[37]. The value of n has increased from 0.35 to 0.92 for bare copper to SAMs covered copper resulting that the copper surface has become smoother due to the formation of dense, non-porous monolayer of 5-methyl-1,3,4-thiadiazole-2-thiol. When the value of n drops to unity slowly, the behaviour of SAMs tend to be an ideal capacitor[38].

The changes in the double layer capacitance and interfacial capacitance have been found to be correlated with SAMs formation. In addition, the polarization resistance, which corresponds to the charge transfer resistance, increases as the coverage increases. Since the double layer capacitance is larger than the capacitance of SAMs, it will dominate the total capacitance as the SAM coverage decreases. The high frequency EIS data is modelled with a Randle's

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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- the capacitance.

In theory the hydrophobic alkanethiol monolayers are ionic insulators[39] and the Nyquist plot appears to be a straight line, But, the studies of Nahir and Bowden[40] have shown that electrons can penetrate SAMs even though they are defect free and more-over SAMs are found to contain molecule seized defects[41-44]. Zamborini and Crooks[41] have 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 and leading to further destruction of SAMs. But hydrocarbons containing nitrogen and sulphur within the SAMs can partially heal the defects. Hence, in such case,
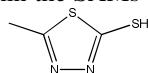
5-methyl-1,3,4-thiadiazole-2-thiol $\{C_3H_4N_2S_2\}$ 5-Methyl-1,3,4-thiadiazole 2-thiol containing two nitrogen and two sulphur atoms, bond tightly to the metal surface thus forms a very thick monolayer that prevents the diffusion of corroding chemicals and ions and offers a great protection for copper from being corroded. And the inhibition efficiency is calculated using the formula,

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

Where, R_t is the resistance of bare copper and R^1_t the resistance of SAMs covered copper. And the results find a very good correlation with polarization and weight-loss studies.

Thus, all the observations in the impedance studies indicate that there is the formation of non-porous, highly protective film(SAM) on the metal surface, which effectively protects the metal from corrosion even in aggressive environment like sodium chloride.

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

Inhibitor	E_{corr} (mv)	I_{corr} ($\mu A/cm^2$)	b_a (mv/decade)	b_c (mv/decade)	IE (%)
Blank1 hr	-101	296	137.02	106.72	-
Thiol film	-26	6.73	168.43	145.62	98
B 2 hr	-125	309.3	139.80	149.39	-
Thiol film	-59	8.24	166.69	218.91	97
B 4 hr	-127	505.7	169.09	141.14	-
Thiol film	-37	4.60	161.52	136.42	99
B 6 hr	-138	508.5	148.87	167.70	-
Thiol film	-23	7.23	178.63	178.63	99

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

Conc.	R_{ct} (KΩ cm^2)	Cdl(μF cm^2)	n	IE (%)
Blank 1 hr	1.36	0.166	0.25	-
Thiol film	19.01	0.0014	0.92	93
B 2 hr	0.222	6.261	0.15	-
Thiol film	18.54	0.0015	0.96	99
B 4 hr	0.198	7.804	0.15	-
Thiol film	26.12	0.00093	0.96	99
B 6hr	0.154	12.867	0.12	-
Thiol film	123.89	0.000058	0.97	100

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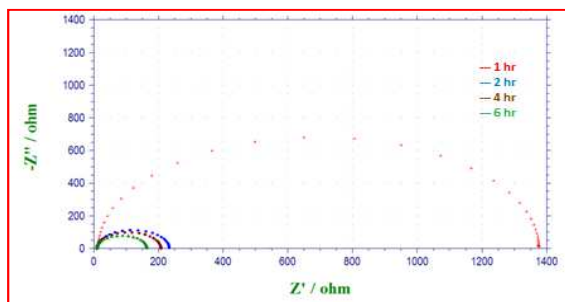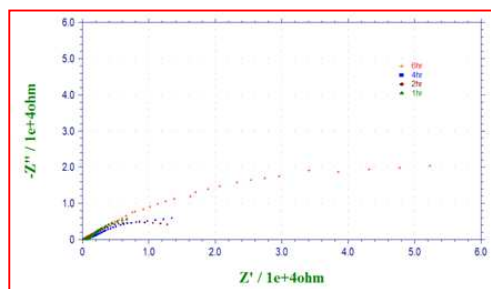| Figure 7.a. | Figure 7.b. |

. Nyquist plots at different immersion periods in aq. 300 ppm chloride a) bare copper b) SAMs covered copper
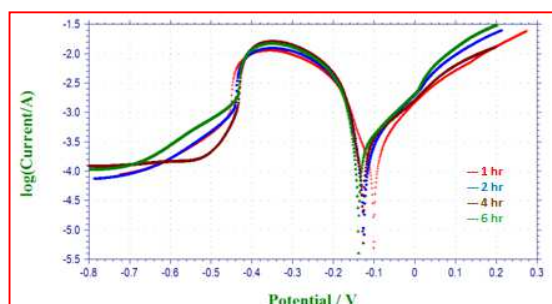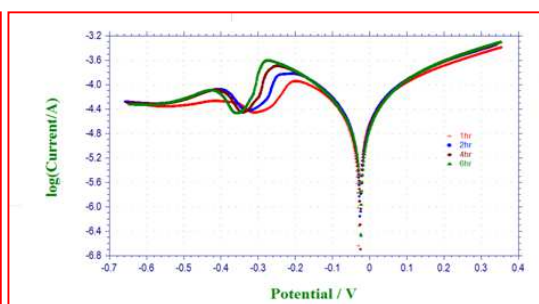

| Figure 8.a. | Figure 8.b. |

Potetiondynamic polarization curves at different immersion periods in aq. 300 ppm chloride a) bare copper b) SAMs covered copper

Table 7. Corrosion parameters obtained from potetiodynamic polarization studies of bare and SAMs covered copper of 5 ppm inhibitor concentration in different concentrations of aq. NaCl. Solution

Inhibitor	E_{corr}(mv)	I_{corr}(μA/cm^2)	b_a mv/decade)	b_c mv/decade)	IE (%)
Blank100 ppm	-94	418.2	187.30	171.43	-
Thiol	+15	6.164	173.52	167.33	99
B 150 ppm	-105	502.5	186.15	175.44	-
Thiol	+5	6.945	164.72	150.96	99
B 200 ppm	-109	491.5	173.34	161.84	-
Thiol	-7	6.754	158.78	148.32	98
B 250 ppm	-138	183.3	175.31	158.77	-
Thiol	-3	7.524	155.01	137.42	96
B 300 ppm	+3	125.4	192.38	189.86	-
Thiol	-25	73.89	191.24	856.16	94

Table 8. Impedance parameters of bare and SAMs covered copper of 5 ppm inhibitor concentration in different concentrations of aq. sodium chloride solution

Conc. (ppm)	R_{ct} (KΩ cm^2)	Cdl(μF cm^2)	n	IE (%)
B 100	0.843	0.4183	0.2	-
Thiol	8.231	0.00456	0.85	90
B 150	0.728	0.5496	0.19	-
Thiol	6.112	0.00804	0.80	88
B 200	0.680	0.6423	0.18	-
Thiol	3.443	0.0255	0.75	80
B 250	0.375	2.050	0.16	-
Thiol	2.339	0.00555	0.77	84
B 300	2.56	0.4	0.35	-
Thiol	55.192	0.000098	0.94	95

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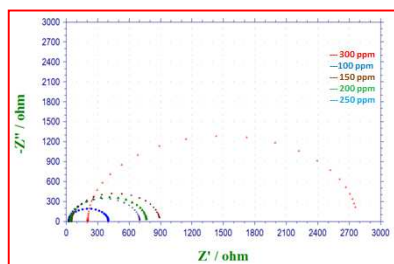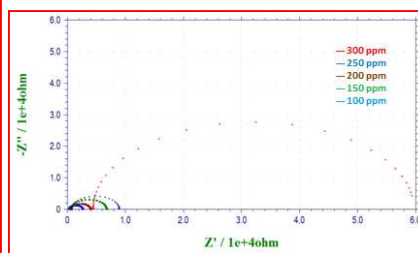**Figure 9.a.**   **Figure 9.b.**
Nquist plots in different concentrations of aq. sodium chloride solution a) bare copper b) SAMs covered copper

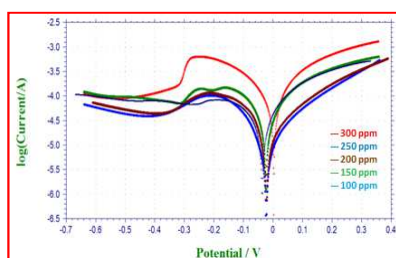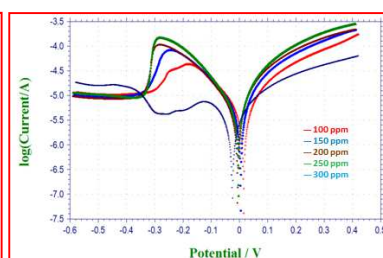**Figure 10.a.**   **Figure 10.b.**
Potentiodynamic polarization curves in different concentrations of aq. sodium chloride solution a) bare copper b) SAMs covered copper

These results are also in good agreement with the results obtained in the literature for different SAMs on copper[45,46].

3.2.4. CV studies:

The cyclic voltammograms of bare and SAMs covered copper for 2 cycles at sweep rate of 100 mV/s and with different sweep rates are shown below. For bare copper there exists two oxidation peaks at 0.140 V (a) and 0.180 V (b) 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 (c) in the reverse scan, which is due to the reduction of $CuCl_2^-$, is shown in **fig. 12.b**. The SAMs covered copper exhibits no oxidation peak and one reduction peak -0.16 V in the reverse scan (a), which is shown in **fig. 11.a**. Compared with bare copper, the anodic and cathodic peak currents of SAMs covered copper have decreased to the maximum from 4×10^{-3} A to 1.8×10^{-4} A for anodic and from -4.8×10^{-3} A to -0.5×10^{-4} A, for cathodic which have a very slight change to -0.6×10^{-4} A even after 15cycles (a), which is not very significant and no oxidation peak even after 15 cycles[47], which is shown in **fig. 11. b**. The larger shifts in the anodic and cathodic peak currents can be due to the formation of complex (of the thiol molecule) with the metal, which inhibited strongly the oxidation of Cu(0) to Cu(I), thus preventing the diffusion of corroding ions. These results infer the stability of thiol film on the copper surface, which provides the evidence for the protection of copper in corrosive sodium chloride environment.
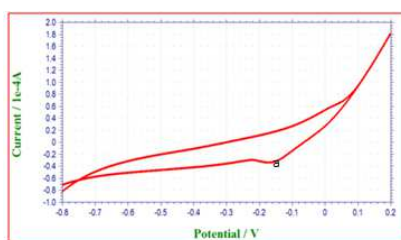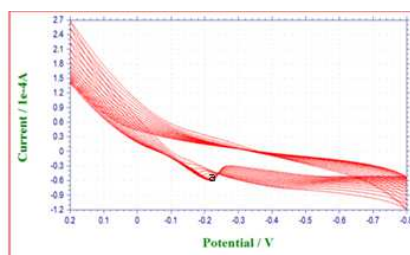

Figure 11.a.   **Figure 11.b.**
Cyclic voltammogram of SAMs covered copper in aq. 300 ppm sodium chloride solution a) at a sweep rate of 100 mV/s/cycle   b) at a sweep rate of 100 mV/s for 15 cycles
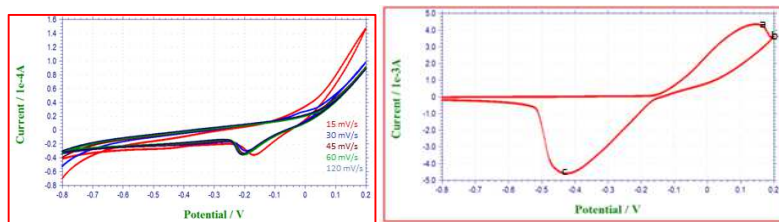
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Figure 12. a.   **Figure 12. b.**

CV in aq. 300 ppm sodium chloride solution a) SAMs covered copper for different sweep rates b) bare copper 100 mV/s/cycle

3.3. Surface characterization studies
3.3.1. Inra-Red Spectroscopic studies

FT-IR spectra for bare and SAMs covered copper are shown below. It shows the appearance of peaks at1485cm^{-1},1614 cm^{-1}, 2922 cm^{-1}, which correspond to C = N, C = C and C - H stretching respectively and also C - N stretching at 1268 cm^{-1} and C – S stretching at 794.5 cm^{-1}[35,45]. These peaks infer the presence of SAMs of 5-methyl-1,3,4-thiadiazole on copper surface. The lowering of C = N stretching from 1600 to 1485 cm^{-1}[46]and of C – N stretching from 1276 to 1268 cm^{-1} refer to the formation of complex between SAMs and copper surface through nitrogen atom. These peaks identified are found to be similar with the peaks of pure thiol which appear at 1465 cm^{-1}, 1637 cm^{-1}, 1271 cm^{-1} respectively, clearly shows the formation of thiol monolayer on the metal surface.. For bare copper, there appear two peaks at 445 cm^{-1} and at 489.5 cm^{-1}, which is assigned to cuprous oxide formed on the surface of the copper metal (Yoshida and Ishida, 1995). Thus, the shifts of the peaks in the spectrum of the surface film recorded in the presence of the inhibitor, when compared to the spectrum of pure compound confirms the complex formation between copper and the inhibitor. Thus, the shift towards lower frequency range shows the adsorption of nitrogen and sulphur, which prevent the attack of corrosive elements mainly like chloride and 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 shift 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 offers a very high inhibiting efficiency.
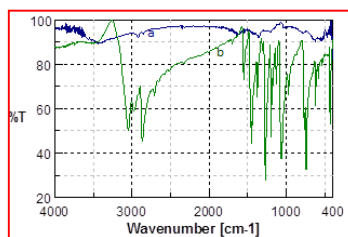

Figure 13. FT-IR spectra of a) SAMs covered copper b) pure thiol

3.3.2. Scanning Electron Microscopic 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 **Figure14.** have showed that most of the area of the bare copper have been corroded due to the adsorption of chloride ions and the surface appears very rough due to the uneven formation of the corrosion products and in **Figure 16.** the SAMs coated copper plates have a smooth uniform coverage of 5-methyl-1,3,4-thiadiazole molecule of 5 ppm concentration, without having any defective site and thus preventing the adsorption of chloride ions. And inhibits 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.
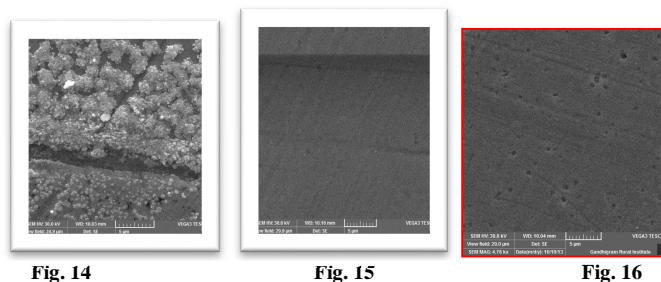
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Fig. 14   **Fig. 15**   **Fig. 16**

SEM images of 14) copper in 300 ppm NaCl 15) SAMs covered copper in 300 ppm NaCl 16) pure copper

3.3.3. Energy Dispersive X-ray analysis

The **figures17. 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 have 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 covers the whole surface forming a uniform protective layer and the absence of corroding elements like chlorine & oxygen prove the dense formation of monolayer offering a very higher inhibition efficiency and prevents the diffusion of corroding elements and isolates copper from corroding environment.
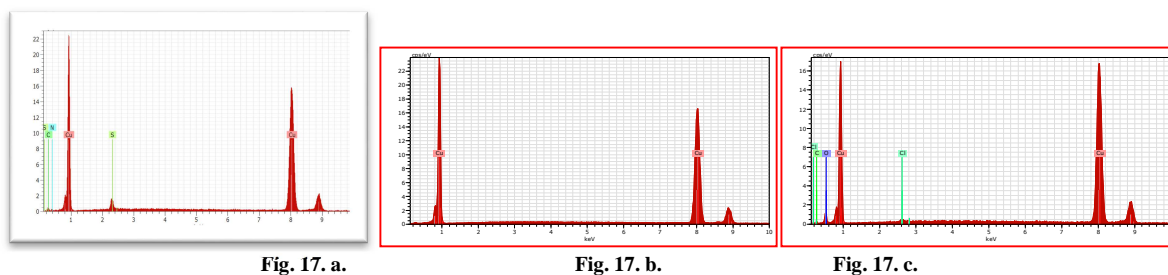

Fig. 17. a.   **Fig. 17. b.**   **Fig. 17. c.**

EDX analysis of a) SAMs covered copper in 300 ppm NaCl b) pure copper c) pure copper in 300 ppm NaCl

3.3.4. Contact angle measurements

Figures 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 104.6^0 and 76.0^0 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 nearly equal with the hydrophobic film of Amino thiol (116.7^0) which offers a very high inhibition efficiency.

Fig. 18.a.   **Fig. 18.b.**

Contact angle images of a) SAMs covered b) bare copper

3.3.5. Atomic Force Microscopic studies

The topography of the surfaces recorded in 2D and 3D images are 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 19.a, b, c** shows the AFM images and cross section analysis of polished copper metal surface, with Ra value of 0.9504 µm, Rms value of 1.404 µm

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indicated 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 of 2.435 µm, Rms value of 2.463 µm indicated the adsorption of chloride ions and the formation of corrosion products. The root-mean-square (RMS) roughness is found to be 2.463 µm, which clearly indicates the roughness of the corroded surface. The microstructure of the surface shows several smaller and larger corrosion product deposits. Whereas the decrease in roughness of the SAMs covered copper surface show the dense, uniform adsorption of thiol on the metal surface**.** The decrease in RMS roughness from 2.463 µm for bare to 2.078 µm for SAMs covered copper clearly infer the greater smoothness and homogeneity of the surface film produced by the thiol monolayer and the absence of any corrosion product deposits, which offers a protective layer thereby, forming a barrier against the attack of aggressive ions from the corrosive environment.
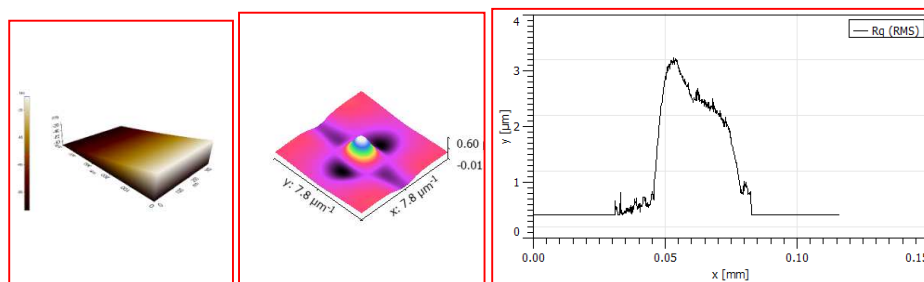

| **Figure 19. a.** | **Figure 19. b.** | **Figure 19. c.** |

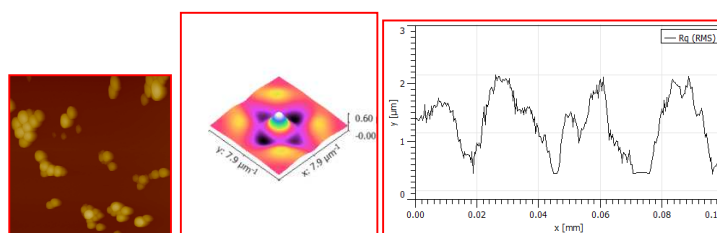**a) 2 D image of polished copper metal b) 3 D image of polished copper metal c) RMS roughness measurement**

| **Fig. 20.a.** | **Fig. 20.b.** | **Fig. 20. c.** |

a) 2 D image of bare copper b) 3 D image of bare copper c) RMS roughness measurement
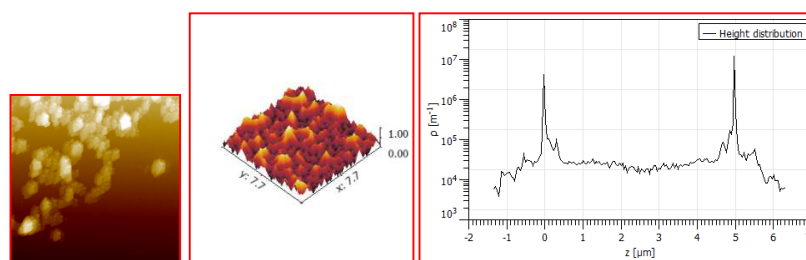

| **Fig. 21. a.** | **Fig. 21.b.** | **Fig. 21. c** |

a) 2D image of SAMs covered copper b) 3 D image of SAMs covered copper c) RMS roughness measurement

Table 9. AFM parameters

Environment	Ra (µm)	Rms (µm)
Polished Cu metal	0.9504	1.404
Polished Cu metal in 300 ppm Cl-	2.435	2.463
SAMs covered metal surface	**1.741**	**2.078**

3.3.6. X-ray Photoelectron Spectroscopic studies

The XPS studies for copper immersed in 300 ppm aqueous chloride environment and copper immersed in the inhibitor solution are carried out. The pattern of the film formed on the surface of copper in the presence and absence of inhibitor are represented below. The peaks due to Cu 2p, C 1s and O 1s electrons are detected in the XPS survey spectrum of bare copper and the corresponding computer deconvolution spectra are shown in **Figures 24.a, b, c, d** respectively. The Cu $2p_{3/2}$ at a binding energy of 936 eV can be attributed to Cu (I) and the binding energy at

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282 eV corresponds to C 1s electron. The O 1s peak at 531 eV could be due to the formation of Cu_2O at the initital stages. The XPS survey spectrum of copper covered with SAMs show peaks due to Cu 2p, O 1s, C 1s, N 1s and S 2p and the corresponding computer deconvolution spectra were shown in **Figures 22.a to f**. The Cu $2p_{3/2}$ peak at 933 eV show the presence of cuprous copper and C 1s peak at 284 eV is due to the presence of carbon atoms in the alkyl chain of methyl thiol. The N 1s peak at 400 eV shows the presence of nitrogen in the third position in thiol molecule, which could be explained as nitrogen in the third position can donate the electron pair easily to form a bond with copper. The S 2 p peak at 164 eV and with the deviation of +1 eV at 163 eV correlated well with the peaks of S available in the literature which is due to the presence of thiolates as discussed in the formation of SAMs on DTA_4, DTA_6, DTA_8. Therefore, the electron density on this nitrogen is reduced and the binding energy is shifted to a higher value of 400 eV from 398 eV[48]. Thus the shift in the elemental binding energies of N 1s revealed the nitrogen atoms present in methyl thiol and sulphur in the methyl thiol SAMs are involved in the complex formation with copper through cuprous ions by chelation(bridge connection)[49]. Since the self-assembled monolayers formed is very thick and dense, it reduces Cu(II) ions formed to Cu(I) ions. And the formation of a thin inhibitor film is in agreement with the SEM observations.
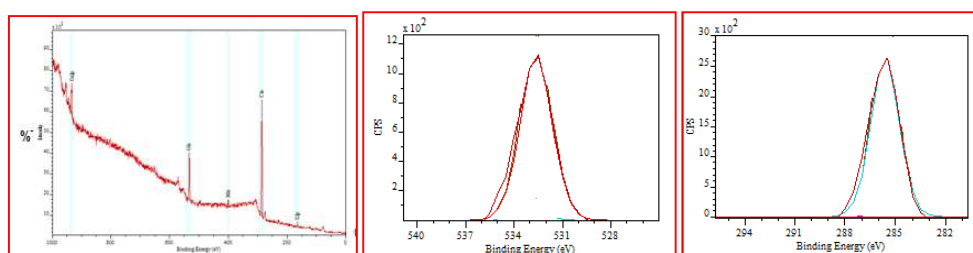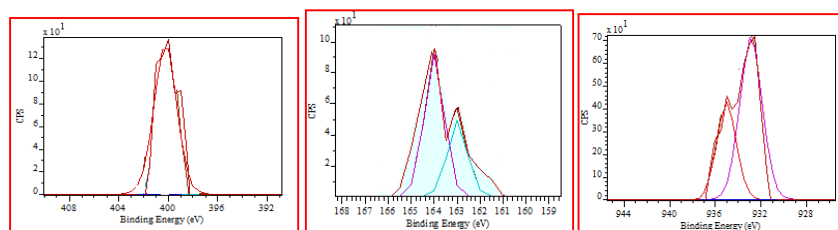

| Fig. 22.a. | Fig. 22.b. | Fig. 22.c. |

| Fig. 22.d | Fig. 22.e | Fig. 22.f. |

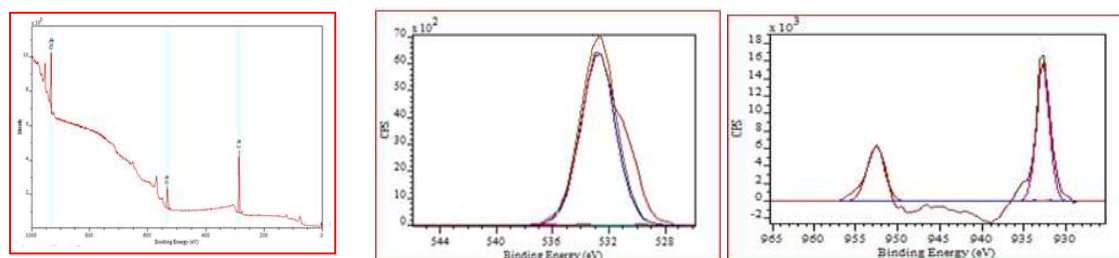**Fig. 22.a, b, c, d, e, f are the XPS survey spectra of SAMs covered copper, deconvolution spectra of O1s, C 1s, N 1s, S 2p. Cu 2p**

| Fig. 23.a. | Fig. 23.b | Fig. 23.c. |

Figures 23.a, b, c are the XPS survey spectra of pure copper, deconvolution spectra of O 1s and Cu 2p
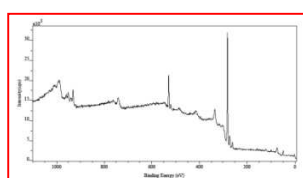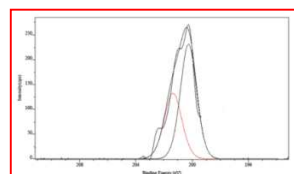

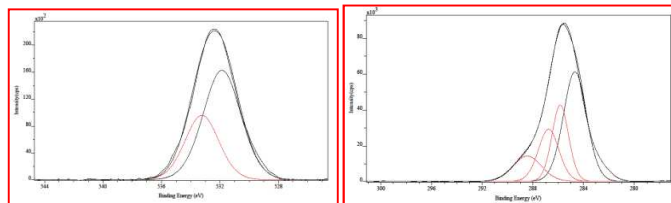| Fig. 24.a. | Fig. 24.b. |

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Fig. 24.c.   **Fig. 24.d.**
Figures 24.a, b, c, d the XPS survey spectra of bare copper, deconvolution spectra of Cl 2p, O 1s, C1s

3.3.7. Mechanism

It is known that the corrosion process of copper in aerated sodium chloride solution comprise the anodic dissolution of copper and cathodic reduction of oxygen[50-52]. The anodic dissolution of copper is shown as,

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

$CuCl + Cl^- \rightarrow CuCl_2^-$
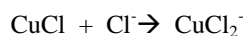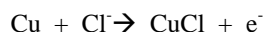
And the cathodic reduction of oxygen is given by,

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

The mechanism involves the formation of a non-porous, dense, protective film on copper surface. Relatively higher contact angle value (104.6^0) of thiol film than bare copper of 76.0^0 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.

CONCLUSION

Therefore it can be 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) 5ppm thiol solution, v) 24hrs immersion , the formation of self-assembled monolayers on copper surface occurs using 5-Methyl-1,3,4-thiadiazole-2-thiol and it offers excellent corrosion protection to copper in sodium chloride environment. And the SAMs molecules get chemisorbed on the copper metal surface and forms co-ordination complex by chelation. The inhibition efficiencies obtained from Polarization, Impedance and Weight-loss studies, offer a very good correlation with each other and CV results proved the stability of SAMs. Hence it is confirmed that the protective monolayer formed on the copper surface plays a very vital role in corrosion inhibition of copper.

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