An Electrochemical and Surface Analysis on Metal by Methyl Para Tollyl Sulphide as Inhibitor in Acidic Media

V. Rethinagiri

Department of Chemistry, M.A.M. College of Engineering & Technology, Trichy, India

ABSTRACT

In this study the inhibitive effect of Methyl Para Tollyl Sulphide (MTS) on metal corrosion in 3M HNO_3 was investigated using weight loss, electrochemical impedance spectroscopy(EIS), and potentiodynamic polarization(PDP). MTS act as an inhibitor for the acid corrosion of metal, Inhibition efficiency of the metal increased with an increase in concentration of MTS but decreased with increase in temperature. The maximum inhibition efficiencies obtained were 93.1%,for weight loss, EIS and PDP technique, respectively. The adsorption of MTS on the metal surface was found to be spontaneous and obeyed Temkin's adsorption isotherm at all studied temperatures. The adsorption is a mixed adsorption involving both chemisorption and physisorption. The metal surface was assessed using scanning electron microscopy (SEM) . Atomic force microscopy(AFM) which also revealed the protective ability of the MTS for metal in HNO_3 solution.

Key words: weight loss , polarization, nitric acid, corrosion inhibitor, SEM

INTRODUCTION

Corrosion is also defined as the loss of useful properties of materials as a result of chemical or electrochemical reaction with its environment. The term corrosion also applies to the degradation of plastics, concrete, ceramics and wood, but generally refers to metals. The well-recognized example of metallic corrosion is the rusting of iron and steel. Besides this there are numerous other familiar examples of corrosion reactions[1-2]. Some of them are tarnishing of silver, dulling of brass, fogging of nickel, etc.   It is now-a-days necessary to pay more attention to metallic corrosion studies than that was done earlier due to · Increasing use of metals in the filed of science and technology. Use of rare and expensive metals whose protection requires special precautions. Use of new high strength alloys which are usually more susceptible to certain type of corrosive attack. Increasing pollution of air and water resulting in a more corrosive environment.· Strict safety standards of operation equipment which may fail in a catastrophic manner due to corrosion.

MATERIALS AND METHODS

2421

Eur. Chem. Bull. 2023, 12(7), 2421-2435

1. Materials

1.1. Preparation of the Copper Specimens

The copper specimens were chosen from the same sheet of the following composition:

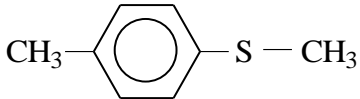| Element	Fe	Cd	Pb	Cu
Composition	0.001	0.01	0.1	99.99

Copper specimens of the dimensions $1.0 \times 4.0 \times 0.25$ cm were polished to mirror finish, degreased with trichloroethylene and used for weight-loss and surface examination studies.

Copper rod encapsulated in Teflon with an exposed cross section of 1 cm^2 area was used as the working electrode in potentiostatic polarisation studies. The surface of the electrode was polished to mirror finish and degreased with trichloroethylene.

1.2. Chemicals Used

The acid solutions (3M HNO_3) were prepared by dilution of an analytical grade HNO_3 with double distilled water. The other chemicals used for the study have been of GR grade. All tests were conducted at different temperatures in magnetically stirred solution.

1.3 Structure and Molecular Formula of Organic Sulphide

1	Methyl Para Tollyl Sulphide (MTS)	C$_6$H$_{10}$S	CH$_3$—⬡—S—CH$_3$

2. Methods

2.1. Weight Loss Measurement

Weight loss measurements were done according to the method described previously[3-5] . Weight loss measurements were performed at 303 ± 1 for 2h by immersing the copper specimens in 3MHNO_3 acid solutions (100 mL) without and with various amounts of inhibitor (0.000001 – 0.01 M). After the elapsed time, the specimen was taken out, washed, dried, and weighed accurately. All the concentrations of an inhibit for weight loss and electrochemical study were taken in molar concentration (M).

2422

The surface coverage (θ) and inhibition efficiency (IE%) were determined by following equations:

$$\theta = \frac{W_0 - W_1}{W_0} \qquad (.1)$$

$$IE(\%) = \frac{W_0 - W_1}{W_0} \times 100 \qquad (.2)$$

where W_1 and W_0 are the weight loss values in presence and absence of inhibitors respectively.

2.2. Weight Loss Measurement at Different Temperatures

The loss in weight was calculated at different temperatures from 303 K to 333 K. Each experiment was duplicated to get good reproducibility. Weight loss measurements were performed in 3M HNO_3 with and without the addition of the inhibitor at their best inhibiting concentration (0.01M). Percentage inhibition of inhibitor at various temperature was calculated.

3. Potentiodynamic Polarisation Measurements

Potentiodynamic polarisation studies have been performed for copper specimen both in the presence and the absence of the inhibitors[5-7].

The electrode used has been a copper rod of the same composition used for weight loss measurement. The specimen has been embedded in PTEF with an exposed area of 1 cm^2. The polarisation cell used has been a three electrode assembly [4, 5]. A rectangular platinum foil has been used as the counter or auxiliary electrode. The counter electrode has a much larger area then the area of the working electrode. This will exert a uniform potential field on the working electrode. The reference electrodes have been $Hg/Hg_2Cl_2/KCl$ for HNO_3 solution.

2.4. Electrochemical Impedance Spectroscopy

Impedance measurements were carried out at the open circuit potential using a computer controlled Solar tron model 1280B potentiostat EIS measurements were carried out in the conventional three-electrode, cylindrical Pyrex glass cell with a capacity of 1000 mL. A Saturated Calomel Electrode (SCE) and a platinum disc electrode were used, respectively, as reference and auxiliary electrodes. The working electrode was embedded in PTFE with an exposed area of 1 cm^2, degreased with AR grade ethanol and acetone, and rinsed with double distilled water before use. All potentials are reported versus SCE, after immersion of the specimen, prior to the impedance measurement, 30 minutes was allowed

2423

Eur. Chem. Bull. 2023, 12(7), 2421-2435

for E_{corr} to attain a stable value before the tests were commenced. The AC frequency range extended from 10 kHz to 0.01 Hz with signal amplitude of 10 mV at the corrosion potential[7-9].

2.7. Scanning Electron Microscopic Studies (SEM)

The copper specimens size of 1 cm^2 were used for surface morphological examination. These copper specimens were immersed in acid containing best inhibiting concentration (0.01M) of inhibitor and uninhibited 3M HNO$_3$ solutions for 2h. They were removed, rinsed quickly with rectified spirit, and dried. Then SEM analysis was performed on HITACHI-model S-3000 H SEM.

2.8 Atomic force microscopy

AFM is a powerful technique for gathering of roughness statistics from a verity of surfaces It is becoming an accepted method of roughness investigation Atomic force microscopy provided direct insight into the changes in the surface morphology takes place at several hundred nanometers when topographical changes owing to the initiation of corrosion and formation of protective film on the metal and presence and absence of inhibitors respectively

## 3.RESULTS AND DISCUSSION

3.1. Weight Loss Studies

Weight loss studies for the aromatic sulphide compounds have been carried out in the concentration range 0.0000001 to 0.01M at 303 K $\pm$ 1 in 3MHNO$_3$ medium and the results are presented in Tables 3.1.The corrosion rate under uninhibited condition has also been given in the same tables. it is observed that sulphide compounds very efficiently reduce the corrosion of copper in 3MHNO$_3$ acid medium and serve as good inhibitor, for the compound it has been found that the efficiency of inhibition increases with increase of inhibitor concentration. This is due to an increase of surface coverage at higher concentration of the additive which retards dissolution of metal. The electron donating nature of sulphur can be attributed for higher inhibition efficiencies

The compound MTS has shown a good performance of inhibition of about 93.96 % in its best protecting concentration in 3MHNO$_3$ medium. The efficiency of more than 80% has been observed at the moderate concentration. *i.e.,* 0.0001M concentration. The lowest concentration of the inhibitor has shown an efficiency of about 50.25 %.

2424

Eur. Chem. Bull. 2023, 12(7), 2421-2435

Table 3.1. **Values of corrosion rate, inhibition efficiency and surface coverage calculated from weight loss method for the corrosion of copper in 3MHNO₃ in the presence of different concentrations of MTS**

Sl.No.	Concentration of Inhibitor (M)	Corrosion Rate (mpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
1	Blank	2.8917	---	---
2	0.000001	1.6201	50.25	0.5025
3	0.000005	1.4671	52.88	0.5288
4	0.00001	1.0220	58.08	0.5808
5	0.00005	0.9191	69.35	0.6935
6	0.0001	0.09092	75.28	0.7528
7	0.0005	0.8235	81.32	0.8132
8	0.001	0.4872	89.92	0.8992
9	0.005	0.2010	90.92	0.9092
10	0.01	0.1799	93.96	0.9396

2425

Eur. Chem. Bull. 2023, 12(7), 2421-2435
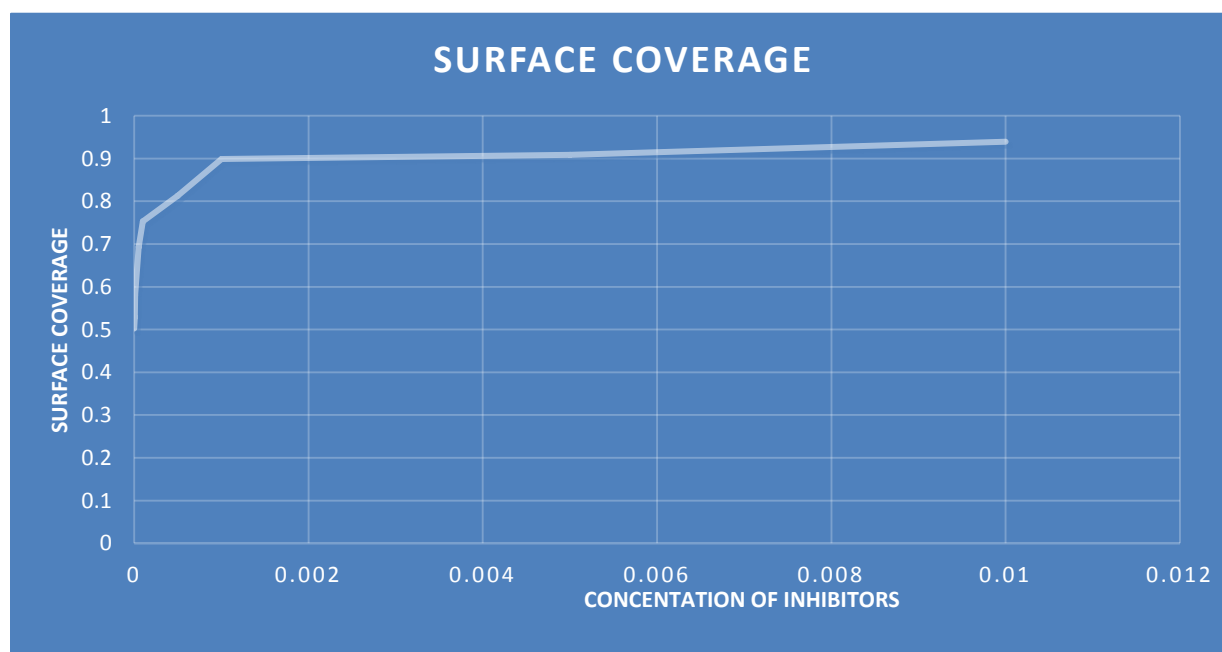
3.2. The Effect of Temperature

The effect of temperature on the inhibition performance of the compound at their best protecting concentration of 0.01M were studied and the results are presented in Table 3.2. . for 3M HNO$_3$ medium.

The compound MTS is able to maintain an inhibition of about 93.96 % at 303 K in 3M HNO$_3$ medium. Thereafter, there is a slow decrease in the efficiency and this is observed up to 323 K. This shows an efficiency of 76 % at 323 K. Thereafter the inhibition declines to 61.2 % at 333 K.

Table 3.2. Values of corrosion rate, inhibition efficiency and surface coverage for different temperatures in the presence of 0.01M concentration of MTS in 3MHNO$_3$

Sl.No.	Temperature (K)	Corrosion Rate	Inhibition Efficiency (%)	Surface Coverage (θ)
1	303	0.1799	93.96	0.9396
2	308	0.2301	90.52	0.9052
3	313	0.2799	87.82	0.8782
4	318	0.3215	81.67	0.8167
5	323	0.4962	76.82	0.7682
6	328	0.5282	69.82	0.6982
7	333	0.3008	61.20	0.6120

2426

3.4. Potentiodynamic Polarisation

The potentiodynamic polarisation measurements carried out for copper in $3MHNO_3$ for different concentrations of the above organic compound is presented in Figure 3.4.

In Figure 3.4 the curves are shifted to lower current regions in the presence of inhibitor showing the inhibition tendency of the organic sulphide compound. There was definite trend observed in the E_{corr} values in the presence of all the sulphide compound., the compound is act as mixed type of inhibitors , but predominantly as cathodic inhibitor .
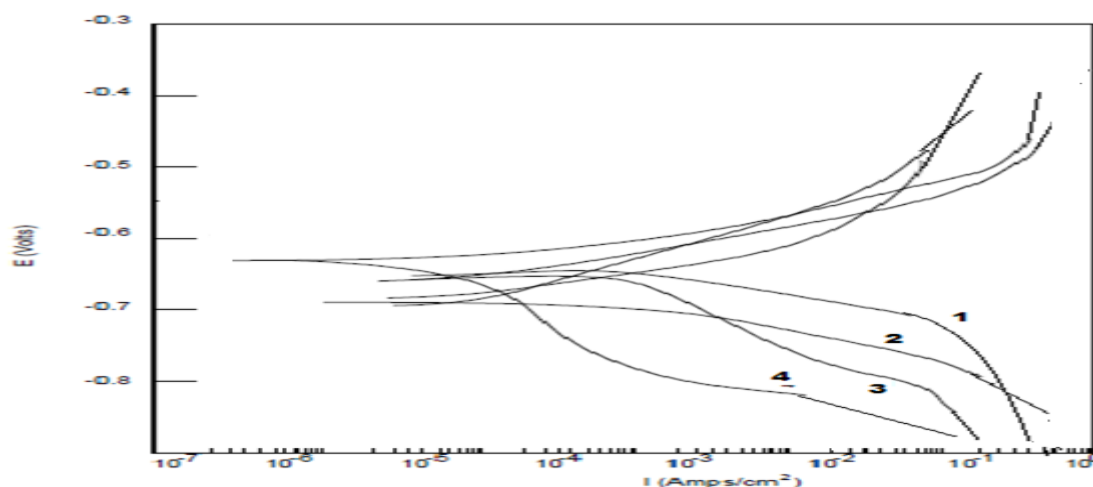
Figure 3.4.Potentiodynamic polarisation curve of copper in $3MHNO_3$ in the absence and presence of various concentrations of MTS

1) **3M HNO₃**

2) **3M HNO₃ + 0.000001M MTS**

3) **3M HNO₃ + 0.0001M MTS**

4) **3M HNO₃ + 0.01M MTS**

The impedance response of copper in acid solution was significant after the addition of all the organic sulphide compound. Furthermore 0.01M concentration of sulphide compound gives rise to much larger semicircle diameter than other two lower concentrations of sulphide compound.

Deviation from perfect circular shape, often known as frequency dispersion, is attributed to surface roughness and in homogeneities of the solid surface . Inspection of the results in 3M HNO_3, indicates that the R_t value increases with the concentration of sulphide compounds. The change of I_{corr} and R_t values can be related to the gradual replacement of H_2O molecule and/or OH^- ions by sulphide compounds on the copper metal surface. The increase in R_t and decrease in I_{corr} values are the formation of protective film on the metal surface.

2427

Moreover the values of C_{dl} decrease with increasing inhibitor concentration. The decrease in C_{dl} is due to the decrease in local dielectric constant and an increase in the thickness of the protective layer at electrode surface.
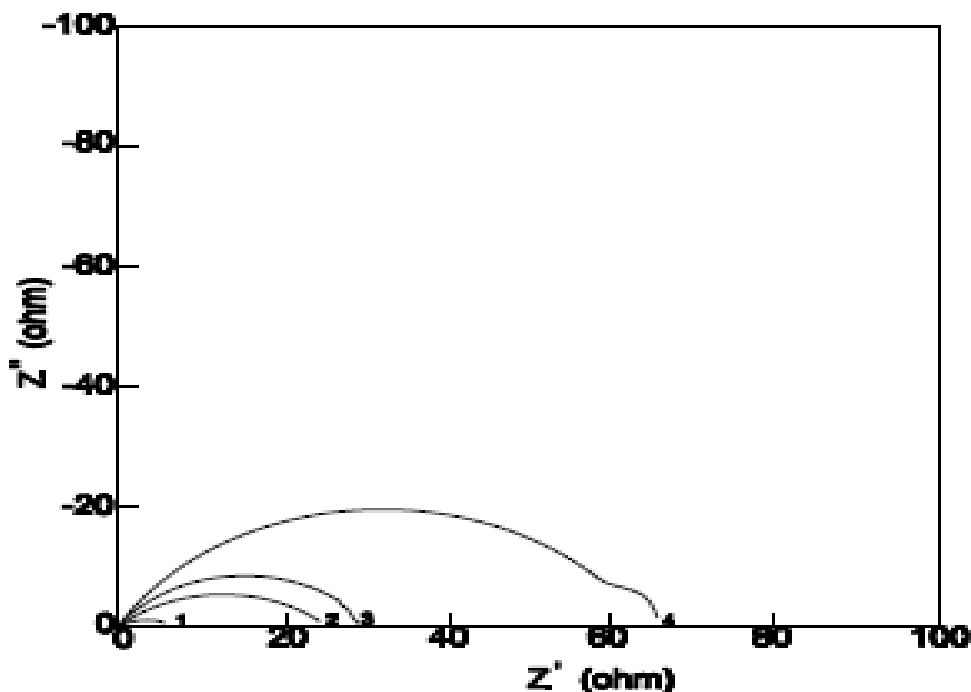

Figure3.5.   Impedance diagram for copper in 3MHNO₃in the absence and presence of various concentrations of MTS

1) 3M HNO$_3$ **2)   3M HNO$_3$ + 0.000001M MTS**

3) 3M HNO$_3$ + 0.0001M MTS   **4)   3M HNO$_3$ + 0.01M MTS**

3.5. Adsorption Isotherm

An adsorption isotherm is the relation that connects the concentration of the organic molecules adsorbed on the electrode surface with the concentration in the bulk at a given temperature.Basic information on the interaction between the inhibitor and copper metal surface can be provided by the adsorption isotherm.

The degree of surface coverage (θ) for different concentration of inhibitors in the acid has been evaluated from weight loss values.   The data were graphically fit to Temkin's Isotherms. Figures 3.6.show the plots of surface coverage (θ) V$_s$ log C and the expected linear relationship is obtained for all the compounds

The very high order of inhibition offered by the sulphide and their high temperature impressive performance confirm the chemisorption of the compound on the metal surface. The

2428

inhibitive action of MTS is attributed to the chemisorption of MTS through the lone pair electron of the sulphur atom.
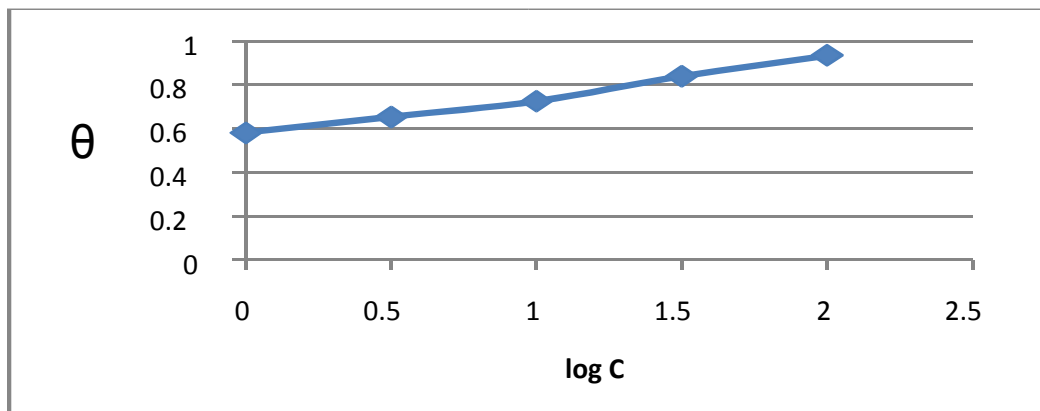

Figure 3.6. **Temkin's adsorption isotherm for copper in 3MHNO$_3$ in the presence of MTS at different concentrations**

3.7. Scanning Electron Microscopy (SEM)

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of copper. The SEM micrographs of the surface are examined. The SEM image of the corroded specimen in the presence of 3M HNO$_3$ solutions is shown in Figure 3.7. The facet seen in the figures is the result of pits formed due to exposure of copper to acid.

The influences of the addition of 0.01 M concentration of MTS, on the copper in 3M HNO$_3$ solutions are shown in Figure 3.8 The facet observed in the blank has disappeared and the surface was smooth and free from pits. It can be concluded that very minimum corrosion occurs in presence of inhibitor and hence corrosion is inhibited in the presence of aromatic sulphid in the acidic medium.
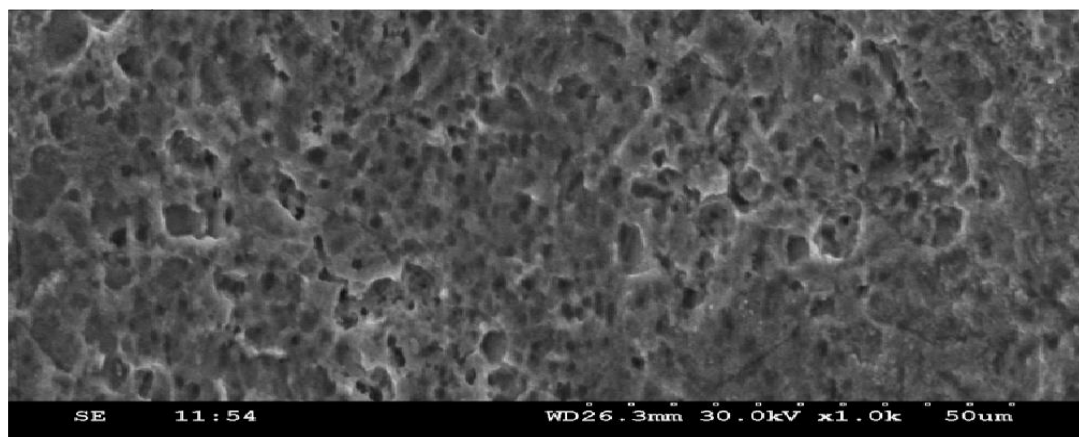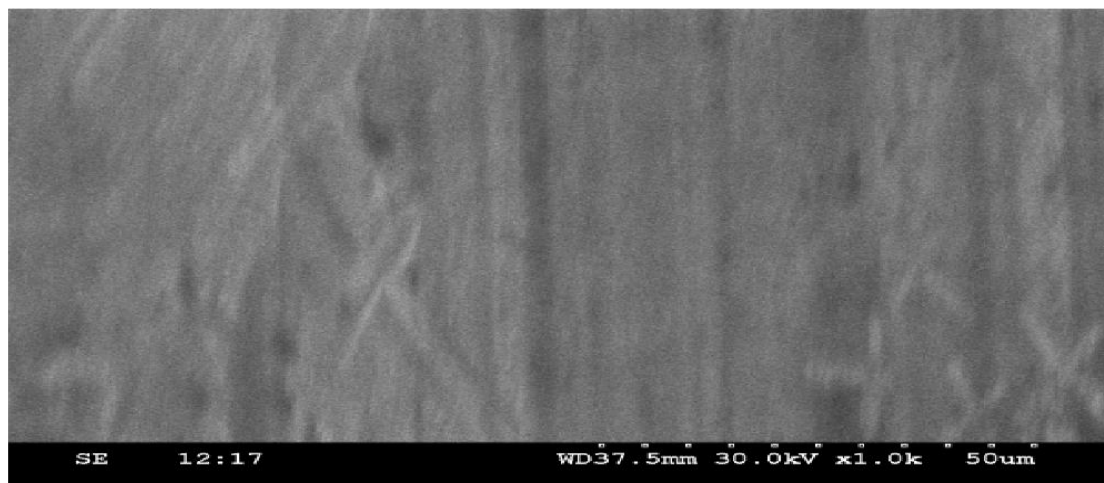

Figure 3.7. **SEM image of copper in 3M HNO$_3$.**

2429

Eur. Chem. Bull. 2023, 12(7), 2421-2435

Figure 3.8.   **SEM image of copper after immersion for 2hr in 3MHNO$_3$ in presence of 0.01M MTS.**

3.8 Atomic force microscopy

All atomic force microscopy images were obtained on a pico SPM2100 AFM instrument operating in contact mode in air. The scan size of all the AFM images an **5 µ m 5 µ m** areas at a scan rate of 2.4 line per second.

The two dimensional (2D) three dimensional (3D) AFM morphologies and the AFM cross sectional profile for polished copper metal surface (reference sample) , copper metal surface immersed in 3M HNO3 (blank sample) and copper metal immersed in 3M HNO containing the   formulation   of **MTS**   are shown in fig (3.9 & 3.9a), (a, d) (b, e)   (c, f) respectively

AFM image analysis was performed to obtain the average roughness **Ra** (the average deviation of all points roughness profile from a mean line over the evaluation length) root mean square roughness , **Rq** (The average of the measured hight   deviations taken within the evaluation length   and measured from the mean line) and tree maximum peak-to-valley **(P-V)** hight values (largest single peak to valley hight in five adjoining sampling hights) **Rq i**s much more sensitive than **Ra** to large and small   hight deviations from the mean

2430

Eur. Chem. Bull. 2023, 12(7), 2421-2435

Table – 3.3 is a summary of the average roughness (Ra) RMS Roughness (Ra) maximum peak-to-valley height (RPV) value of copper surface immerged in different environments.

Sample	RMS(**Ra**) Roughness (nm)	Average(**Ra**) Roughness (nm)	MaximumPeak-to-Valley Hight(nm) **Rpv**
Polished Copper Metal (Control)	0.019	0.016	0.06300
Copper Metal Immersed in 3MHNO$_3$	125.19	113.38	431.900
Copper metal immersed in 3HNO$_3$ containing **MTS.** (100 mM)	48.78	42.45	166.290

The value of **Rq , Ra, Rpv** hight for the polished copper metal surface [reference sample] are 0.019 nm, 0.016nm, and respectively, which shows a more homogeneous surface with some places in where the hight is lower than the average depth fig(a,d) displays the uncorroded metal surface. The slight roughness observed on the polished copper metal surface is due to atmospheric corrosion.

Fig(3.9) 2D and cross sectional profiles of AFM images of the surface a.polished copper metal

b. copper metal immersed in3M HNO$_3$. (blank)

2431

Eur. Chem. Bull. 2023, 12(7), 2421-2435
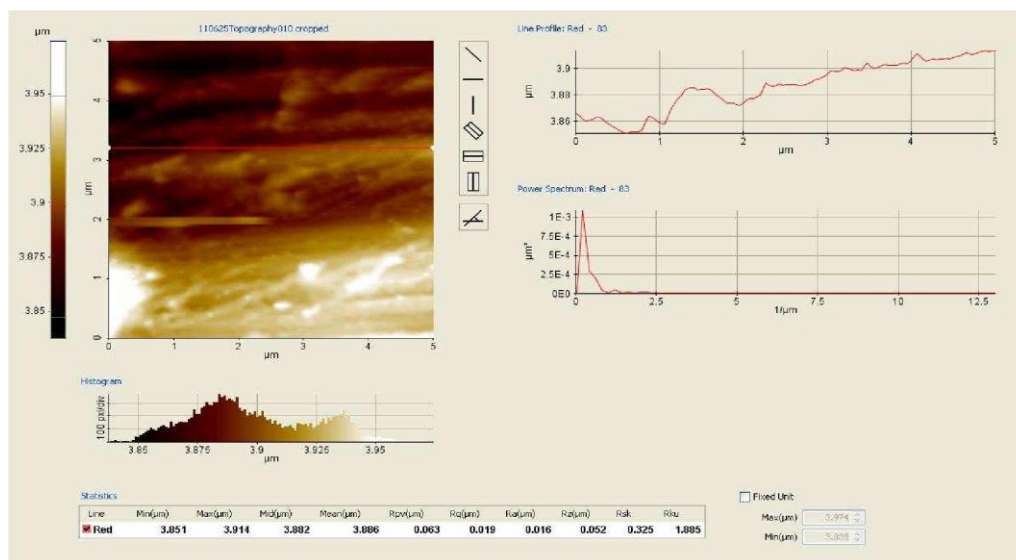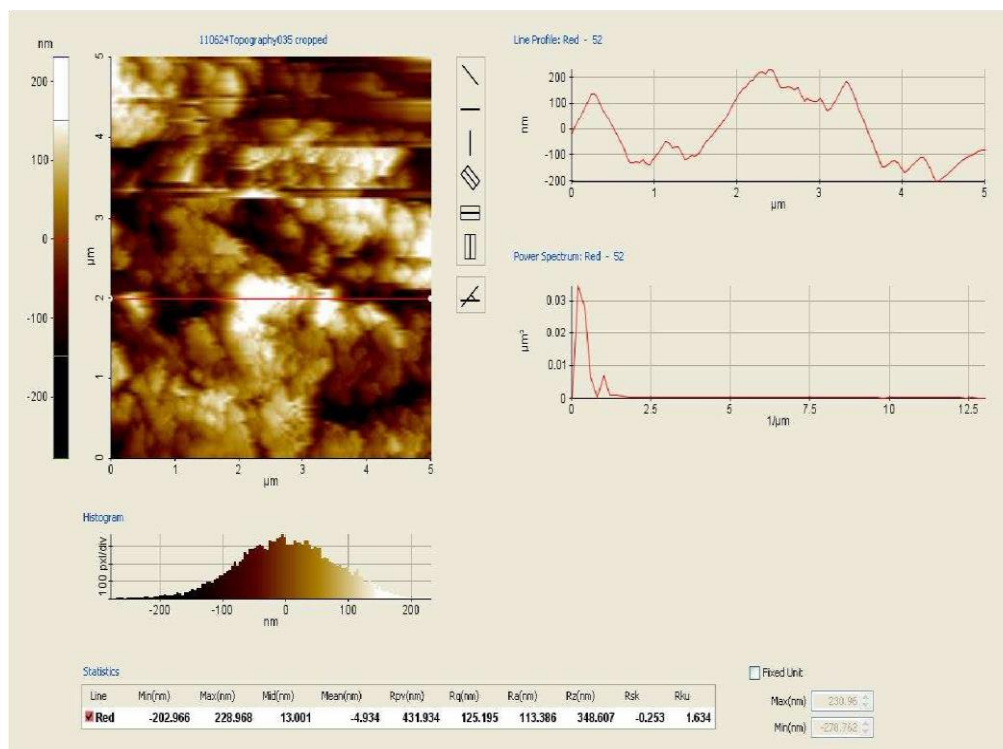
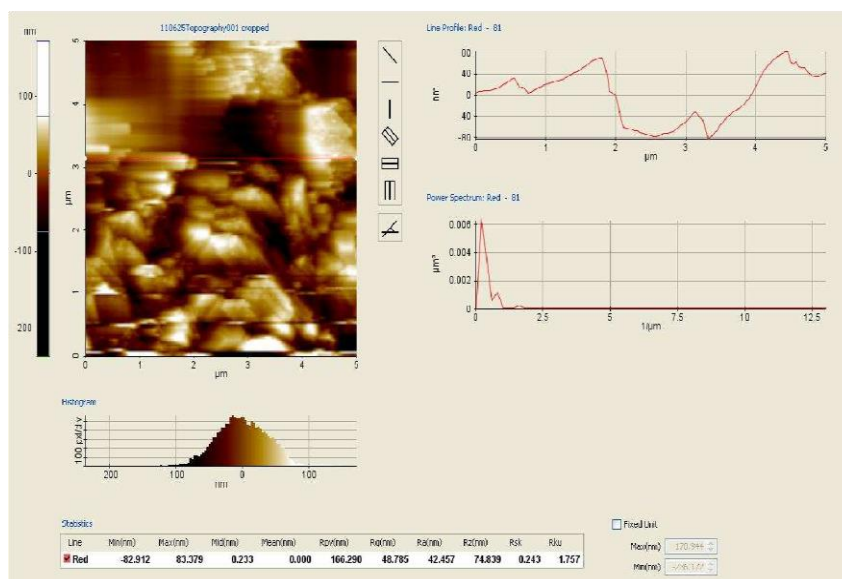c. copper metal immersed in 3M HNO_3 Containing **MTS.**

Fig (3,9a) 3D AFM images of the surface d. polished copper metal

2432

Eur. Chem. Bull. 2023, 12(7), 2421-2435
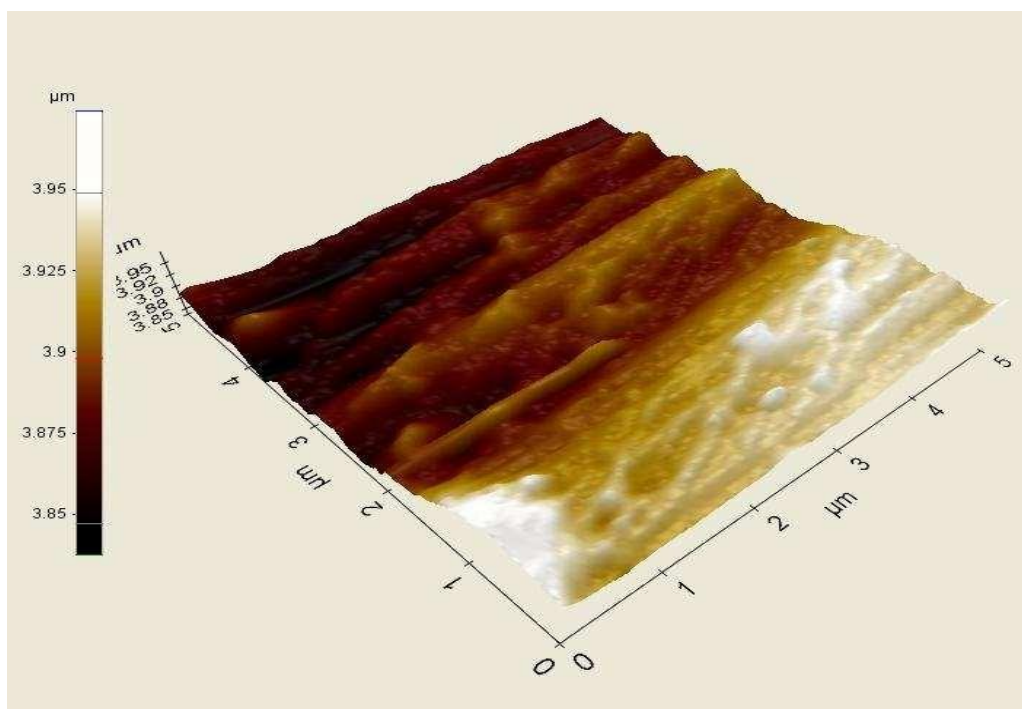
e. copper metal immersed in3M HNO$_3$. (blank)

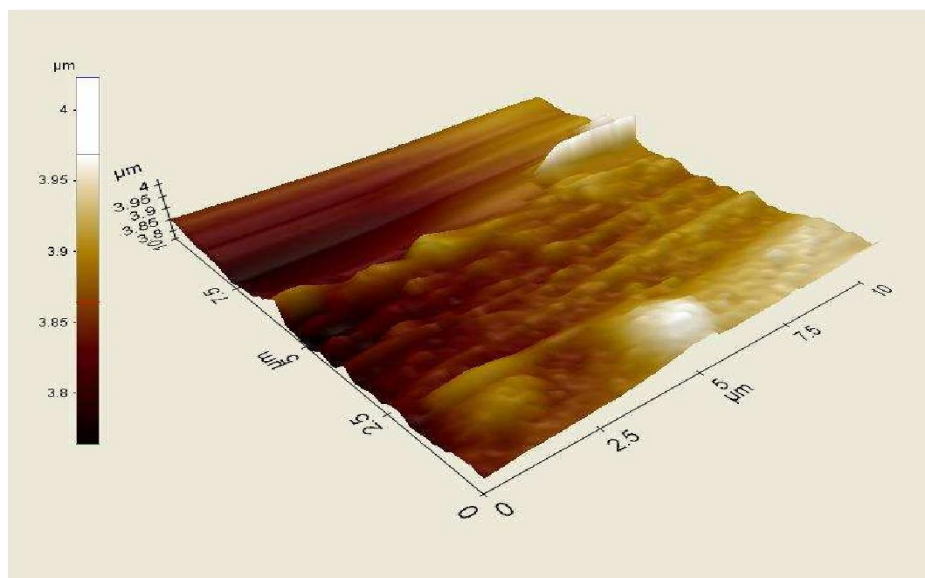f. copper metal immersed in3M HNO$_3$. Containing **MTS.**

2433

Eur. Chem. Bull. 2023, 12(7), 2421-2435
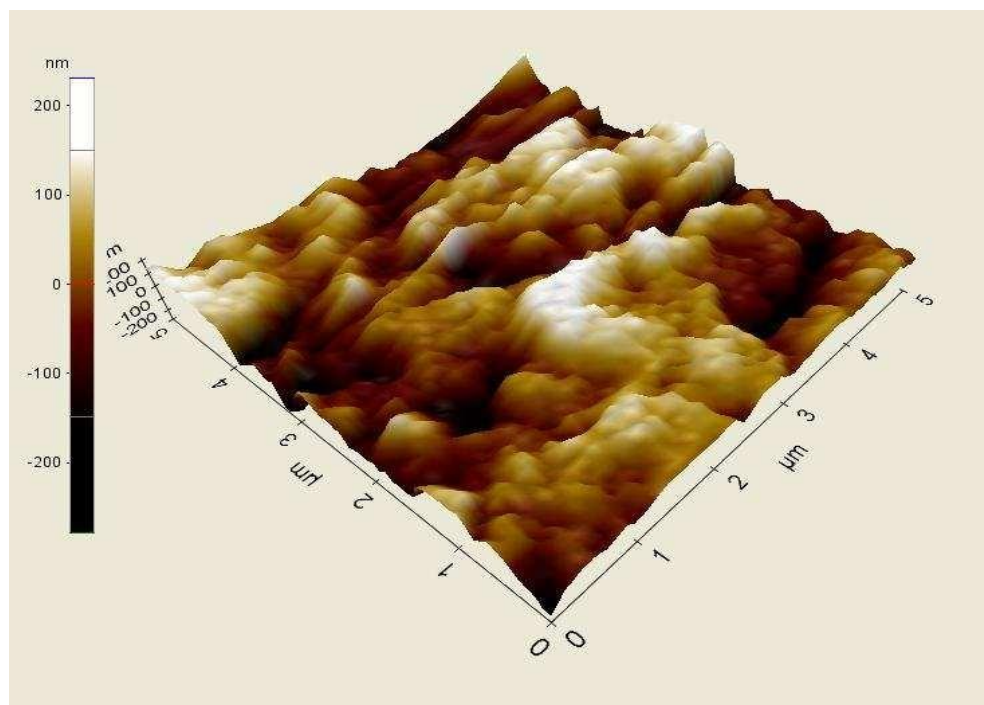
The RMS roughness average roughness and **Rpv** hight values for the copper metal surface immersed in 3MHNO$_3$ are 125.19 nm, 113.38 nm, and 431.900 nm respectively. These date suggests the copper metal surface immerged in 3MHNO$_3$ has a greater surface roughness than the polished metal surface .Which shows that the unprotected copper metal surface is rougher and was due to the corrosion of copper metal in 3MHNO$_3$ fig(b, e) display corroded metal surface with few pits.

The presence of MTS in 3MHNO$_3$ reduces the **Rq** to 48.78 nm from 125.19 nm, and the average roughness is significantly reduce 42.45 nm when compared with 113.38 nm of copper metal surface immersed in 3MHNO$_3$. The maximum peak-to-valley Hight also was reduced to 116.290 nm. These parameters confirm that the surface appears smoother, The smoothness of the surface is due to the formation of compact protective film of **MTS.** on the metal surface there by inhibiting the corrosion of copper metal.

The above parameters observed for copper metal are somewhat greater than the AFM data is polished metal surface which confirms the formation of the film on the metal surface which is protective in nature.

CONCLUSION

On the basis of the above results the following conclusion can be drawn.

- Results obtained from the experimental date shown that **MTS** acts as an effective inhibitor for corrosion in nitric acid.
- The corrosion process was inhibited by adsorption of the organic matter on the copper surface

2434

Eur. Chem. Bull. 2023, 12(7), 2421-2435

- Inhibition efficiency increases with increase in the concentration of the **MTS** but decrease with rise in temperature.
- The adsorption of **MTS** on copper surface from 3MHNO$_3$ obeys Temkin adsorption isotherm.
- Polarization measurements show that **MTS** acts essentially as a mixed type inhibitor.
- The values impedance parameters justify the impressive performance of organic sulphide good corrosion inhibitor.
- The compound bring down the extent of hydrogen permeation through copper in 3M HNO$_3$.
- The SEM &AFM images confirm the formation of protective layer on the metal surface.

REFERENCES

[1]. A. Goswami "Thin film Fundamentals" New Age international (p) Ltd Publishers (1996).

[2] A.K. Jonscher and R.M. Hill, "Physics of Thin films", Vol 8. Academics Press, New York (1978).

[3] X.S. Du, Y.J. Su, J.X. Li, L.J. Qiao, W.Y. Chu" Inhibitive effects and mechanism of phosphates on the stress corrosion cracking of brass in ammonia solutions" Corrosion Science, 2012. 60, 69-75.

[4] . S. Goidanich, J. Brunk, G. Herting, M.A. Arenas, I. Odnevall Wallinder. Atmospheric of brass in outdoor applications Patina evolution, metal release and aesthetic appearance at urban exposure conditions. Science of the Total Environment, 2011. 412-413, 46-57

[5] V. Rethinagiri, M.M.Senthamilselvi, M.Gunasekaran, R.Karthikeya, Investigation and inhibition of Brass in sulphuric acid solutions by 3-Amino 1,2,4 Triazole compound. Int .chem.Tech research. 2014. 67, 3791-3798.

[6] Hongqiang Fan, Shuying Li, Zongchang Zhao, Hua Wang, Zhicong Shi, Lin Zhang. Inhibition of brass corrosion in sodium chloride solutions by self-assembled silane films. Corrosion Science, 2012. 53, 4273-4281.

[7] Milan M. Antonijevic´, Snezˇana M. Milic´, Marija B. Petrovic´" Films formed on copper surface in chloride media in the presence of azoles" Corrosion Science, 2009. 51, 1228-1237.

[8] Ping Qiu, Christofer Leygraf. Initial oxidation of brass induced by humidified air" Applied Surface Science, 2011. 258 1235-1241.

[9] M.B. Valcarce, M. Vázquez. Phosphate ions used as green inhibitor against copper corrosion in tap water' Corrosion Science, 2010. 52, 1473-1420.