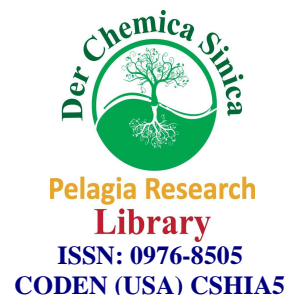




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Corrosion inhibition of copper in acid medium using a new organic sulphide compound

A. J. Abdul Nasser^a, V. Rethina Giri^{b*}, S. Karthikeyan^c, K. N. Srinivasan^d and R. Karthikeyan^a

^a*P.G. and Research Department of Chemistry, Jamal Mohamed College, Tiruchirapalli, India*

^b*Department of Chemistry, J.J. College Engineering and Technology, Tiruchirapalli, India*

^c*Department of Chemistry, Materials Division, VIT University, Vellore, India*

^d*Industrial Metal finishing Division, Central Electrochemical Research Institute, Karaikudi, India*

ABSTRACT

In this study the inhibition effect of Benzyl phenyl sulphide on copper corrosion in 3M HNO₃ solution was studied. Using Electrochemical techniques such as potentio dynamic polarization, Electrochemical impedance spectroscopy (EIS), weight loss (WL), AFM analysis and hydrogen permeation studies to asses the effectiveness of the inhibitor to be used in pickling baths. Results showed that BPhs has good inhibition efficiency on the corrosion of copper in 3M HNO₃ solution. The adsorption of organic compounds on the copper metal surface from the acid follows Temkin's adsorption isotherm and also AFM image analysis was performed to obtain the average roughness from 2D and 3D morphologies.

Keywords: Nitric acid, Weight loss, corrosion inhibition, Atomic force microscopy(AFM), Electrochemical impedance spectroscopy (EIS).

INTRODUCTION

The development of corrosion inhibitors based on organic compounds has much scope in several industries because of their practical usefulness. The molecules structure of organic used as inhibitors has been found to exert a major influence on the extent of inhibition of corrosion[1-4], copper and its alloys are widely used materials for their excellent electrical and thermal conductivities in many applications and recently in the manufacture of integrated circuits[5-6] copper is relatively noble metal, requiring strong oxidants for its corrosion. The chemical dissolution and electronic plating are the main processes used in the fabrication of electronic devices. The most widely used nitric acid solution, so this medium has induced a great deal of research on copper[11-19]. Corrosion most of the effective organic inhibitors have hetero atom such as O,N, S Containing multiple bonds in their molecules through which they can adsorb on the metal surface, In the present study a organic sulphids as inhibitions for the corrosion of copper in 3M HNO₃ have been examined using weight loss measurement. Polarization studies AC impedance Measurements, AFM process through copper in 3M HNO₃ has also been studied and results are reported and discussed.

MATERIALS AND METHODS

Materials and reagents

Copper strips of size 4 X 1 X 0.25 cm and having the percentage composition 99.5% of Cu, 0.001 % of Ni, 0.019% of Al, 0.004 % of Mn, 0.116% of Si and balance impurities were used for electrochemical and gravimetric analysis, the copper samples were mechanically polished using different grades of emery sheets, washed with trichloroethylene and triply distilled water and dried.

The organic sulphides used in this study were procured from Fluka AG, Switzerland, Analar grade HNO₃ was used for preparing the aggressive solution.

METHODS

Weight loss measurements

Weight loss measurement weight loss measurements were called out described in an earlier work [9] copper metal strip was immersed in 100ml of inhibited and uninhibited solutions of 3M HNO₃ for 2 hours. The inhibition efficiency was calculated from weight loss values obtained in the present and absence of the inhibitors at the end of definite intervals of time

$$I E \% = \frac{W_0 - W_i}{W_0} \times 100$$

Where

W₀ = weight loss in plain acid

W_i = weight loss in inhibited acid

Temperatures Effects:

The some procedure adopted for weight for studies at temperature of the study was varied from 35^oc to 60^o. At the end of each experiment. The specimens were taken out washed both in running tap water and in distilled water. They were dried and their weights were measured. The loss in weight was calculated. Each experiment was duplicated to get good reproducibility. Weight loss measurement were performed in 3M HNO₃ with and without the addition of the inhibitor at their best inhibitory concentration percentages inhibitor at various temperature was calculated.

Polarization measurements:

The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential was obtained. Both anodic and cathodic polarization curves were recorded by potentiodynamically (1mVs⁻¹) [7 – 15] using a corrosion measurement system consisting of a BAS Model 100 K H Z to 10MHZ a comprised electrochemical analyzer (made in Lafayette, in USA) PL-10 digital plotter (DMP -40 series the instruments, Division, Houston, TX, USA) made by a platinum for and Hg/Hg₂Cl₂ / 3M HNO₃ were used as the auxiliary electrode and reference electrode respectively. Which was controlled by a personal computer.

EIS measurements:

The electro chemical impedance spectroscopy were carried out using a transfer function analyzer, with a small amplitude ac. The double layer capacitance (C_{dl}) and the charge transfer resistance (R_t) were obtained using ac impedance instrument Princeton Applied Research (Model – 7310). As described in an earlier publications [12-15].

Hydrogen permeation study:

The Hydrogen permeation study was carried out using on adaptation of modified Devananthan and Stachurski's, two compartment cell as described elsewhere [11] Hydrogen permeation current were obtained in the absence and presence of organic sulphide used in the present study.

Adsorption isotherm

The adsorption isotherm can be determined by assuming that inhibition effect is due mainly to the adsorption at metal /solution interface. Basic information on the adsorption of inhibitors on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm the fractional surface coverage values (θ) as a function of inhibitor concentration must be obtained. The values of θ can be easily determined from the weight loss

measurements by the ratio. % I.E /100, where % I E is inhibition efficiency obtained by weight loss method. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitors on the copper surface.

Atomic Force microscopy

AFM is a powerful technique for gathering of roughness statistics from a variety of surfaces AFM is becoming an accepted method of roughness investigation[31-32]

Atomic force microscopy provided direct insight into the changes in the surface morphology that 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

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 are $5 \mu\text{m} \times 5 \mu\text{m}$ areas at a scan rate of 2.4 line per second

RESULTS AND DISCUSSION

Molecular structure of organic compound used in the present study is given in Fig (1)

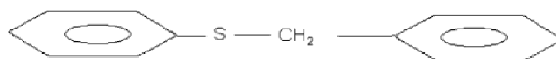
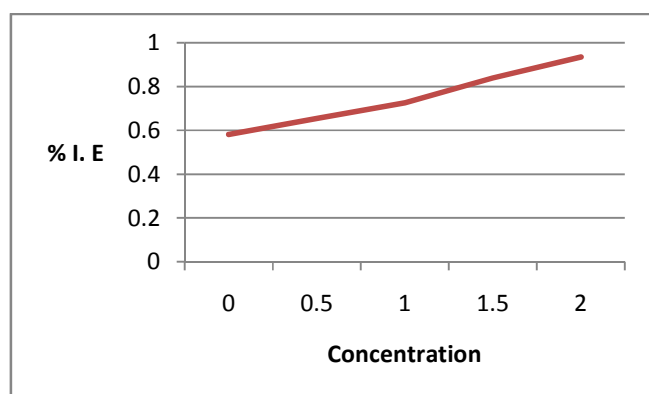


Fig (1) Benzyl Phenyl Sulphide(BPhS)

Table- 1 Corrosion parameters for copper in aqueous solution of 3 M HNO₃ in absence and presence of different concentration of Bphs in 3 M HNO₃ at 30° C for 2 hrs. θ

Inhibitor	Concentration(mM)	% I. E	θ
Blank	3 M HNO ₃	-	-
Bphs	1 mM	58.1	0.581
	5 mM	65.3	0.653
	10 mM	72.5	0.725
	50 mM	83.9	0.839
	100 mM	93.4	0.934

Fig (2) Variation of inhibition efficiency on copper with different concentration of Bphs in 3 M HNO₃ at 30° C for 2 hrs



Weight loss measurements

The value of percentage inhibition efficiency (% I E) and corrosion rate (CR) obtained from weight loss method at different concentrations of Bphs in 3M HNO₃ at 303K are summarized in Tables-1.

The variation of inhibition efficiency with an increase in inhibitor concentrations is shown in Fig (2). It was observed that Bphs inhibits the corrosion of copper in HNO₃ solution at all concentrations used in study, i.e from 1 mM to 100

mM maximum inhibition efficiency was shown at 100mM concentration of the inhibitor . in 3M HNO_3 at 303k. it is evident from table – 1 that the corrosion rate is decreased on the addition of Bphs.

Temperatures Effects:

The value of inhibition efficiency obtained from weight loss measurement at the different temperatures of 303k to 333k in 3M HNO_3 solution at its best protecting concentration are presented in the Tables – 2. The inhibition efficiency decreased at high temperature.

Table- 2 Corrosion parameters for copper in aqueous solution of 3 M HNO_3 in absence and presence of optimum concentration of Bphs at different temperature in 3 M HNO_3 for 2 hrs

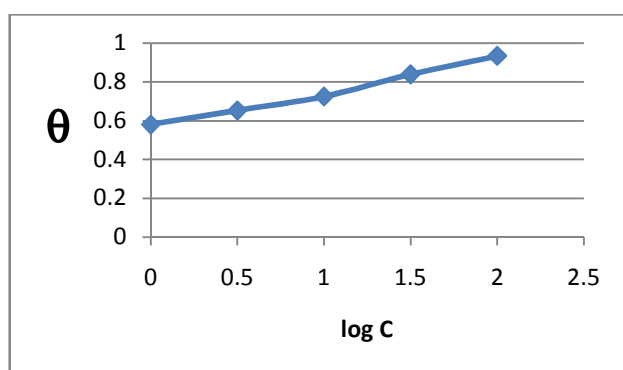
Temperature (K)	Inhibitor	W (mg/cm ² .h)	% I. E
303	Blank	0.3932	-
	Bphs	0.0769	80.8
313	Blank	0.3124	-
	Bphs	0.0244	75.18
323	Blank	0.5723	-
	Bphs	0.0336	65.80
333	Blank	1.2031	-
	Bphs	0.5344	55.58

Adsorption isotherm

The adsorption isotherm can be determined by assuming that inhibition effect is due mainly to the adsorption at metal /solution interface. Basic information on the adsorption of inhibitors on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm the fractional surface coverage values (θ) as a function of inhibitor concentration must be obtained. The values of θ can be easily determined from the weight loss measurements by the ratio. % I.E /100, Where % I.E is inhibition efficiency obtained by weight loss method. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitors on the copper surface.

The values of surface coverage (θ) for different concentration of inhibitors in 3M HNO_3 Solution were evaluated from weight loss measurement the data were tested graphically by fitting to various isotherms including Frumkin Langmuir and Temkin's a straight line relationship was obtained. When θ is plotted against $\log c$ for various concentrations of inhibitors suggesting that the adsorption isotherm relationship as shown in the fig (3) from this we can say that the inhibitors adsorption on the it is assumed that the adsorption of inhibitors at the metal solution interface is the first step in the action mechanism of inhibitors in aggressive acid medium.

Fig 3 Temkin's adsorption isotherm plots for copper in 3 M HNO_3 containing Bphs for 2 hrs



Potential dynamic polarization measurement :

Current – potential characteristics resulting from cathodic and anodic polarization curves of copper in 3M HNO_3 in the presence and absence of Bphs at various concentrations are presented in Table – 3 gives values of corrosion current (I_{corr}) corrosion potential (E_{corr}) cathodic Tafel slope (b_a, b_c mv / dec) for Bphs at various concentration in 3M HNO_3 In the case of polarization method the relation determines the inhibition efficiency (% I.E)

$$\% \text{ I E} = \left(1 - \frac{I_{\text{corr}}^0}{I_{\text{corr}}}\right) \times 100$$

Where I_{corr}^0 and I_{corr} are the uninhibited and inhibited corrosion current densities

Table- 3 Corrosion kinetic parameters obtained from potentiodynamic polarization studies for copper in aqueous solution of 3 M HNO₃ in absence and presence of different concentration of Bphs.

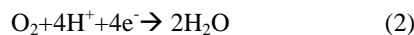
Inhibitor	Concentration(mM)	E_{corr} (Mv)	Tafel slops(mv/dec)		I_{corr} (mA Cm ⁻²)	% I. E
			ba	bc		
Blank	3 M HNO ₃	-925	70	130	3.800	-
Bphs	10	-920	80	149	1.0070	73.6
	50	-905	83	154	0.6080	84.0
	100	-888	86	180	0.2622	93.1

As it is shown in Tables - 3, cathodic current – potential curves give rise to parallel Tafel lines indicating that the hydrogen evolution reaction is under activation controlled the cathodic current density decreases with the concentration of Bphs more over a small effect is observed on the anodic portions. This result indicates that Bphs is adsorbed on the metal surface on the cathodic sites and hence inhibition occurs, we remark that the inhibitor acts on the anodic portion and the anodic current density is reduced

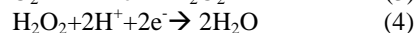
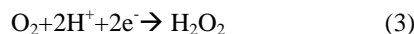
It seems also that the presence of the inhibitor change slightly the corrosion potential values in no definite direction. These results indicated that Bphs acts as a mixed type inhibitor.

The pure HNO₃ and Bphs containing nitric acid solutions used in our experiments were all aerated where dissolved oxygen may be reduced on copper surface and this will allow some copper corrosion to occur [16-18]

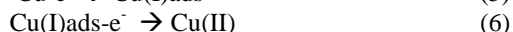
It is a good approximation to ignore the hydrogen evolution reaction and only consider oxygen reduction in the aerated nitric acid solution at potentials near the corrosion potential[19] cathodic reduction of oxygen can be expressed either by a direct 4e⁻ transfer Eq(2)



Or by two consecutive 2e⁻ steps involving a reduction to hydrogen Eq (3) followed by a reduction according to Eq(4)



The transfer of O₂ from the bulk solution to the copper solution interface will strongly affect rate of oxygen reduction reaction.



Where Cu(I)ads is an adsorbed species at the copper surface and does not diffuse into the bulk solution[21-22] The dissolution of copper is controlled by the diffusion of soluble Cu(II) species from the outer Helmholtz plane to the bulk solution.

Upon addition of Bphs it is obvious that slopes the anodic and cathodic Tafel lines remain unchanged. Giving rise to a nearly parallel set of anodic lines and an almost parallel cathodic lines same.

The adsorbed inhibitor decrease the surface area for corrosion without affecting the corrosion mechanism of copper in these solutions, and only causes inactive part of the surface with respect to the corrective medium.[25-25]

Electrochemical Impedance spectroscopy

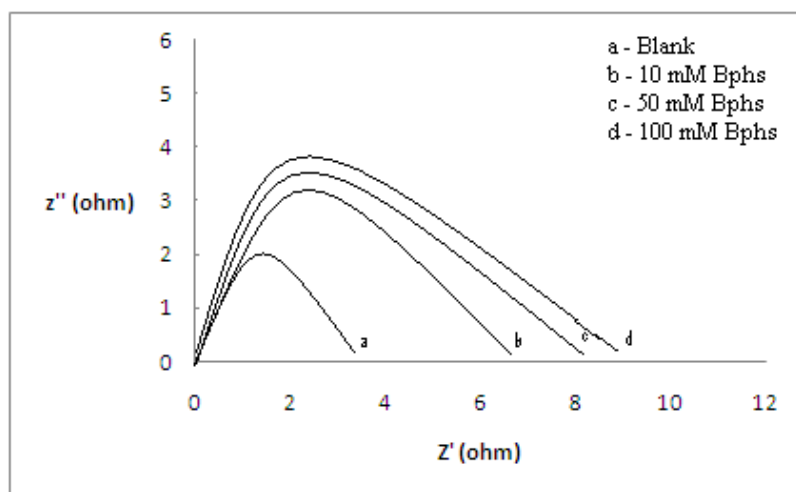
The results of impedance parameters (R_t and C_{dl}) for inhibitors are given in Table - 4 and fig (4). It can be seen from the Table - 4 that the charge transfer resistance (R_t) value increase with increase in inhibitor concentrations but the value of double layer capacitance (C_{dl}) decrease due to decrease in local dielectric constant and increase in

thickness of the electrical double layer, suggesting that the inhibitor molecules function by adsorption at the metal solution interface. Hence the inhibition efficiency increases with increase in inhibitor concentration. This may be due to the availability of more sites on the metal surface in 3M HNO₃ solution because of the lesser adsorption of the sulphide ions on the metal surface.

Table- 4 Impedance parameters for the corrosion of copper in 3 M HNO₃ in absence and presence of different concentration of Bphs

Inhibitor	Concentration(mM)	Rt Ω Cm ²	C _{dl} μ Cm ⁻²	I _{corr} (mA Cm ⁻²)	% I. E
Blank	3 M HNO ₃	4.7	183.2	3.500	-
Bphs	10	50.2	99.0	0.9210	73.0
	50	56.9	58.9	0.5792	82.9
	100	77.4	52.9	0.2399	93.0

Fig 4 Impedance diagram for corrosion of copper in 3 M HNO₃ in absence and presence of different concentration of Bphs.



The variation of permeation current against time for copper metal in 3M HNO₃ solution in the absence and presence of inhibitors. The inhibitors bring down the permeation currents effectively and their corresponding percentage are shown in Table-5. The order of the reduction in permeation current is same as the order of extent of corrosion inhibition. The reason for the best performance of Bphs is due to enhance cathodic polarization to a greater extent than anodic polarization. So it is found to enhance the energy barriers for the proton discharge which leads to less permeation of hydrogen through the copper metal

Atomic Force microscopy

AFM is a powerful technique for gathering of roughness statistics from a verity of surfaces AFM 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

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 \times 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 HNO₃ containing the formulation of Bphs are shown in fig (5 & 5a), (a, d) (b, e) (c, f) respectively

Root Mean square roughness average roughness and peak –to-valley value;

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 height deviations taken within the evaluation length and measured from the mean line) and tree maximum peak-to-valley (**P-V**) height values (largest single peak to valley height in five adjoining sampling heights) **Rpv** is much more sensitive than **Ra** to large and small height deviations from the mean [31]

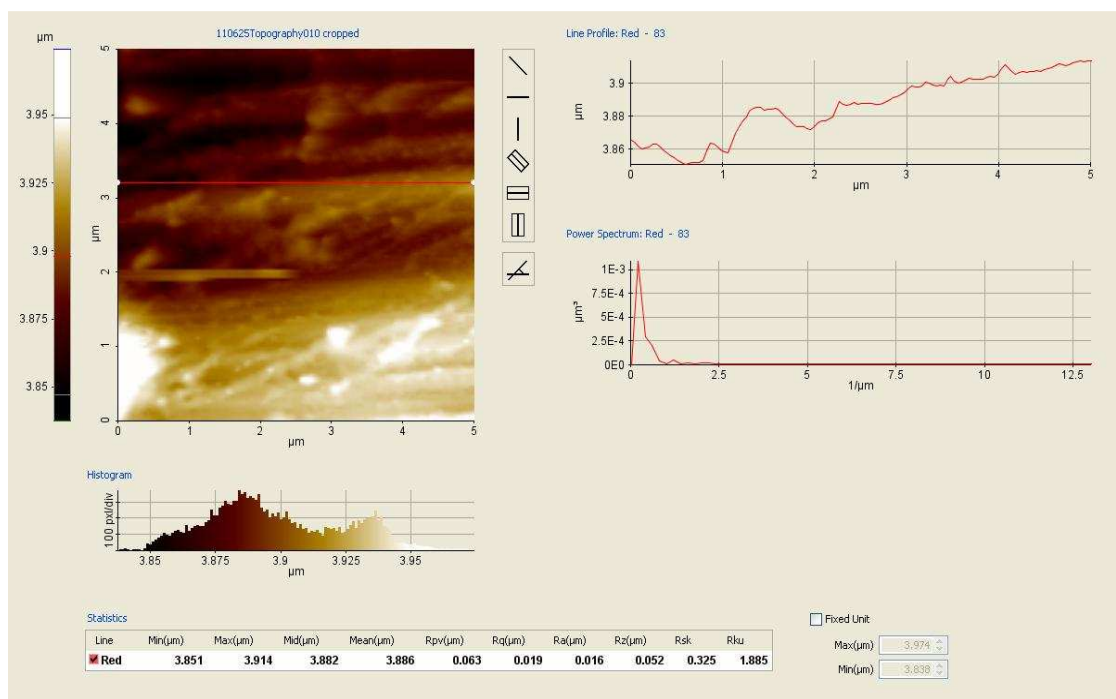
Table - 5 is a summary of the average roughness (Ra) RMS Roughness (Ra) maximum peak-to-valley height (RPV) value of copper surface immersed in different environments.

Table - 5 AFM data of copper metal surface immersed in inhibited and uninhibited environment

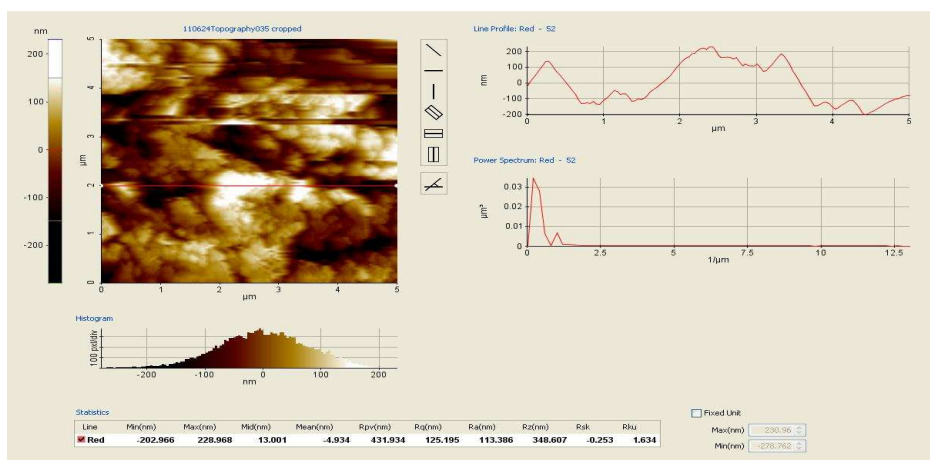
Sample	RMS(Ra) Roughness (nm)	Average(Ra) Roughness (nm)	MaximumPeak-to-Valley Hight(nm) Rpv
Polished Copper Metal (Control)	0.019	0.016	0.06300
Copper Metal Immersed in 3MHNO ₃	125.19	113.38	431.900
Copper metal immersed in 3HNO ₃ containing Bphs(100 mM)	48.78	42.45	166.290

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(5) 2D and cross sectional profiles of AFM images of the surface
a.polished copper metal**



b. copper metal immersed in 3M HNO₃. (blank)



c. copper metal immersed in 3M HNO₃. Containing Bphs

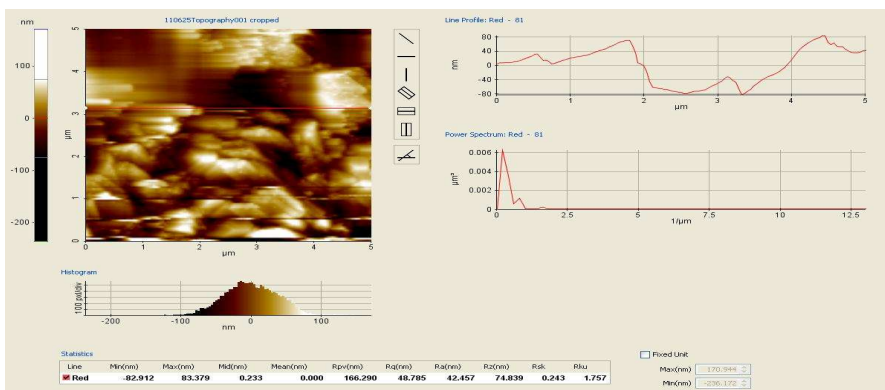
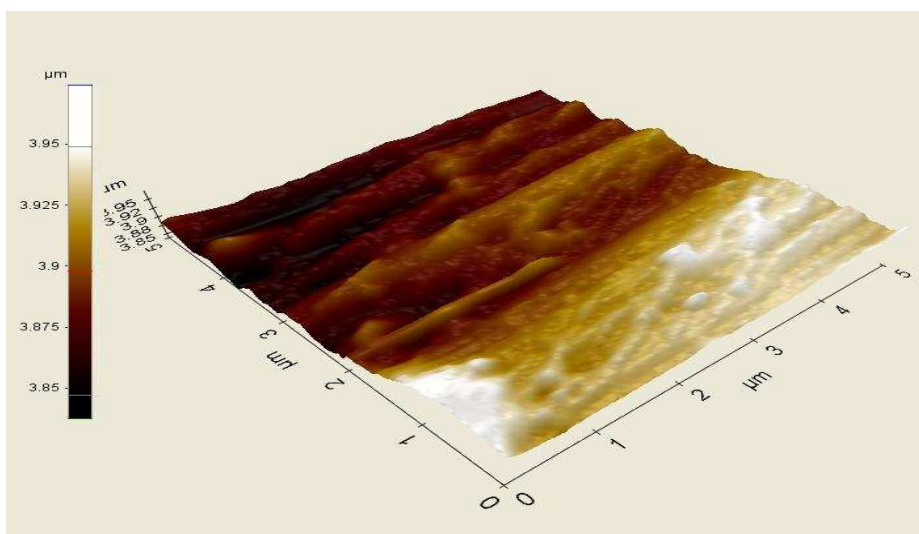
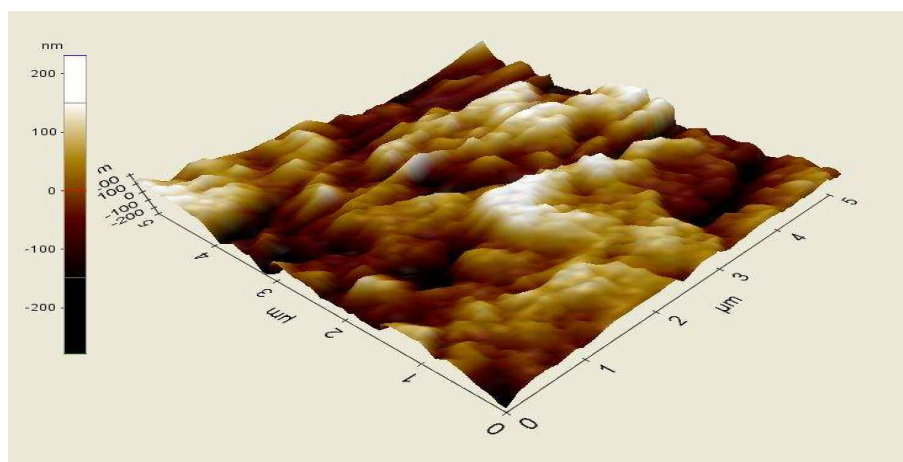
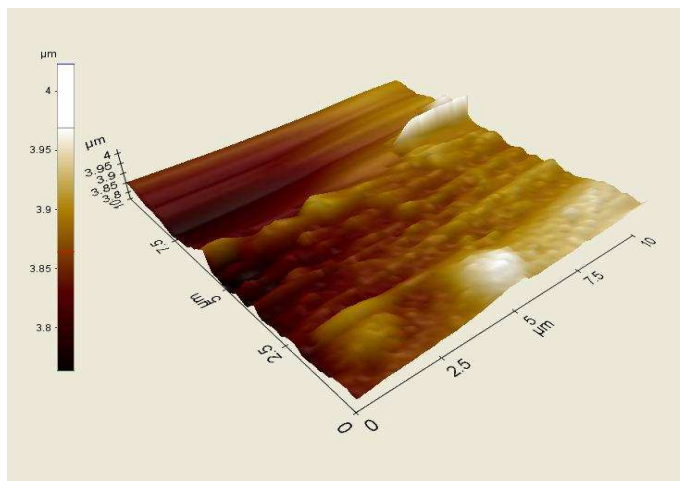


Fig (5a); 3D AFM images of the surface d. polished copper metal



e. copper metal immersed in 3M HNO₃. (blank)**f. copper metal immersed in 3M HNO₃. Containing Bphs**

The RMS roughness average roughness and **R_{pv}** height values for the copper metal surface immersed in 3MHNO₃ are 125.19 nm, 113.38 nm, and 431.900 nm respectively. These data suggests the copper metal surface immersed in 3MHNO₃ 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 3MHNO₃. fig(b, e) display corroded metal surface with few pits.

The presence of Bphs in 3MHNO₃ reduces the **R_q** 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 3MHNO₃. The maximum peak-to-valley height 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 Bphs 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 Bphs 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
- Inhibition efficiency increases with increase in the concentration of the Bphs but decrease with rise in temperature.
- The adsorption of Bphs on copper surface from 3MHNO₃ obeys Temkin adsorption isotherm.
- Polarization measurements show that Bphs 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 HNO₃.
- The AFM images confirm the formation of protective layer on the metal surface.

Acknowledgement

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REFERENCE

- [1] C.E.Ho, W.T.Chen, C.R.Kao, *J Electron Mater.*, **2001**,30 ,399.
- [2] F.Bentigs, M. Lebrini, and M. Lagrenee, *CorrosSci.*, **2005**,47,2955.
- [3] A.J. Abdul Nasser, M.Annarsathiq, *Bull.ElectroChem .*, **2007**, 23,237.
- [4] H.Y.Tsai, S.C.Sun, S.J.Wang, *J ElectrochemSoc.*, **2007**,147,2766.
- [5] V.Oteino-Alergo, N. Huynh, T.Notoya , S.E.Bottle, D.P Schwewinsberg, *Corros.Sci*, **1999**,41 ,685.
- [6] A.Krishnamoorthy, K.Chanda, S.P. Murarka, G.Ramanath, J.G.Ryan, *Appl.PhysLett.*, **2001**,78, 2467-2469.
- [7] S.Barnatt, *Electro Chem. Acta .*, **1970** ,10,1313.
- [8] S.Barnatt, *S.Corrosion.*, **1971**, 27, 467.
- [9] J.C. Jeeva, G.Bech Nelson, *CorrosSci.*, **1973**,13,351.
- [10]M.A.V. Devanathan, Z.Stachurski, *Proc. Roy Soc .*,**1962** ,270A, 90.
- [11]] F.Mansfeld , *Corrosion .*, **1981**,37,301.
- [12] F.Mansfeld , M.W.Kedig, S.Tsai, *Corrosion.*, **1982**, 38,570.
- [13] W.J.Lorenz , F.Mansfeld, *Corros Sci.*, **1981**, 21, 647.
- [14] I.Epelvoin, M.Keddam, H.Aknouti, *J.Appl. Electrochem .* **1972**,2,71.
- [15]S.H. Glarum . J.H. Marshal, *J.Electrochem.Soc.*, **1979**,126 , 24.
- [16] R.Schumacher, A.Muller and W.Stockel, *J.Electroanal. chem .*, **1987**,219,311.
- [17] W.D. Bjorndahl and K.Nobe, *Corrosion .*, **1984**,40, 82.1.
- [18] G.Quartarone, G.Moretti, T.Bellomi, G.Capabianco and A.Zingales, *Corrosion.*, **1998**,54,606.
- [19] P.Jinturkar, Y.C.Guan and K.N. Han, *Corrosion.*, **1984**,54, 106.
- [20] T.Hurlen, G.Ottesen and A.staurset, *Electro.chem .Acta .*, **1978**,23, 23.
- [21] R.Caban and T.W.Chapman, *J.Electrochem .Soc .*, **1977**,124,1371.
- [22] K.F.Khaled and A.M. Amn .*Corros.sci*, **2009**, 51, 2098.
- [23] J.W.Schlitz and K.Wippermann, *Electrochim.Acta .*, **1987**,32,823.
- [24] H.Ashassi-sorkhabi, N.Ghalabsaz-Jeddi, F.Hashemzadeh, H.Jahani, *Electrochim. Acta.,*, 2006, 51,3848.
- [25] O.Zarrouk, B.Hammouti, H.Zarrok, M.Bouchrine, K.F.Khaled, S.S.Al-Deyab *int.J.Electrochem.Sci.*,**2012**,7, 89-105.
- [26] A.Fiala, A.Chibani, A.Darchan, A.Boulkamh, K.Djebbar, *Appl.Surf.Sci.*, **2007**,253,9347.
- [27] M.A.Quraishi, D.Jamal, *Corrosion.*, **2000**, 56, 156.
- [28] M.S.El.Sayed,R.M.Erasmus, J.D. Comins, *J.Colloid Interface.sci.*,**2007** ,311 144.
- [29] L.MalkiAlaoui, B.Hammouti, A.Bellaouchou, A.Benbachir, A.Guenbour, S.Kertit, *Der Pharma Chemica.*, **2011**,3,353.
- [30] Z.Khiati, A.A. Othman, M. Sanchez-Moreno, M.C.Bernard, S.Joiret, E.M.M Sutter, V.Vivier, *Corros.Sci*, **2011**,53,3092.
- [31] BenitaSherine,A.Jamal Abdul Nasser, S.Rajendran., *International journal of engg.sci.and.Tech.* vol .,**2010**,2(4),341-357.
- [32] C.Amra, C.Deumic, D.Torricini, P.Roche, R.Galindo, P.Dumas and F.Selvan, *Greroble, proc. SPIE.*, 1994, 2253, 614-630.

- [33] Kalada Hart, N C Oforka and A O James, *Advances in Applied Science Research*, **2011**, 4, 14-20.
[34] Lakshmi Prabha .K, Shameela Rajam, Venkatraman B. R. *Der Chemica Sinica*, **2012**, 3 (1):158-164.
[35] Baban K. Magarea and Milind B. Ubaleb. *Der Chemica Sinica*, **2011**, 2 (2):158-164.
[36] Yadav. M. Debasis Behera and Usha Sharma. *Der Chemica Sinica*, **2012**, 3(1):262-268.