

Investigation of the inhibition of copper corrosion in nitric acid solutions by organic sulphide compound

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ABSTRACT

The inhibition effect of the addition of organic compounds containing a sulphur group such as Diethyl sulphide (DES) on the corrosion of copper in nitric acid was studied by weight loss and polarization techniques, results obtained revealed that the organic compound is good inhibitor. Polarization studies showed that the compound is mixed type inhibitor. The adsorption of the inhibitor on the copper surface was given by Temkin's adsorption isotherm. The effect of temperature on the corrosion behavior of copper in nitric acid in presence of definite concentration of the inhibitor was studied in the temperature range 30-60^oc. The SEM examination of the copper surface revealed that the compound prevented from corrosion by adsorption on its surfaces.

Key words: copper, polarization, nitric acid, corrosion inhibitor, SEM.

INTRODUCTION

Copper is extensively used in various industrial operations and the study of its corrosion inhibition is of grate importance, most investigations on the corrosion of copper have been carried out on. The development of corrosion inhibitor based on organic compounds has much scope in several industries because of their practical usefulness. The molecular structure of organic compounds used as inhibitor 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 electro 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 [11-16]. Most of the effective organic inhibitor 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 organic sulphids as inhibitions for the corrosion of copper in 3M HNO₃ have been examined using weight loss measurement, Polarization studies and SEM process [1, 9] and results are reported and discussed.

The aim of the present investigation was to study the inhibitive action of organic compounds on the corrosion of copper in the 3M nitric acid solution.

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 chemical analysis, the Copper samples were mechanically polished using different grades of emery sheets, washed with trichloroethylene and triply distilled water and dried.

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

Methods

Weight loss measurements

Weight loss measurement was carried out in a 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 presence and absence of the inhibitor at the end of definite intervals of time.

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

Where

W₀ = weight loss in plain acid

W_i = weight loss in inhibited acid

Temperatures Effects

The same procedure adopted for weight loss for studies at temperature of the study was varied from 30^oC to 60^oC 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 was performed in 3M HNO₃ with and without the addition of the inhibitor at various temperatures was calculated.

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 inhibitor 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 inhibitor on the copper surface.

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 – 16] using a corrosion measurement system consisting of a BAS Model 100 KHz 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. This was controlled by a personal computer.

Scanning Electron Microscope

The copper immersed in blank and in the inhibitor solution for a period of 2 hours was removed, rinsed with double distilled water, dried and observed in a Scanning Electron Microscope to examine the surface morphology. The surface morphology measurements of the copper were examined using Hitachi S-3000 computer controlled Scanning Electron Microscope.

RESULT AND DISCUSSION

Molecular structure of organic compound used in the present study is given in

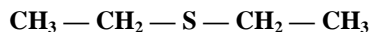


Fig (1) Diethyl Sulphide (DES)

Weight loss measurements

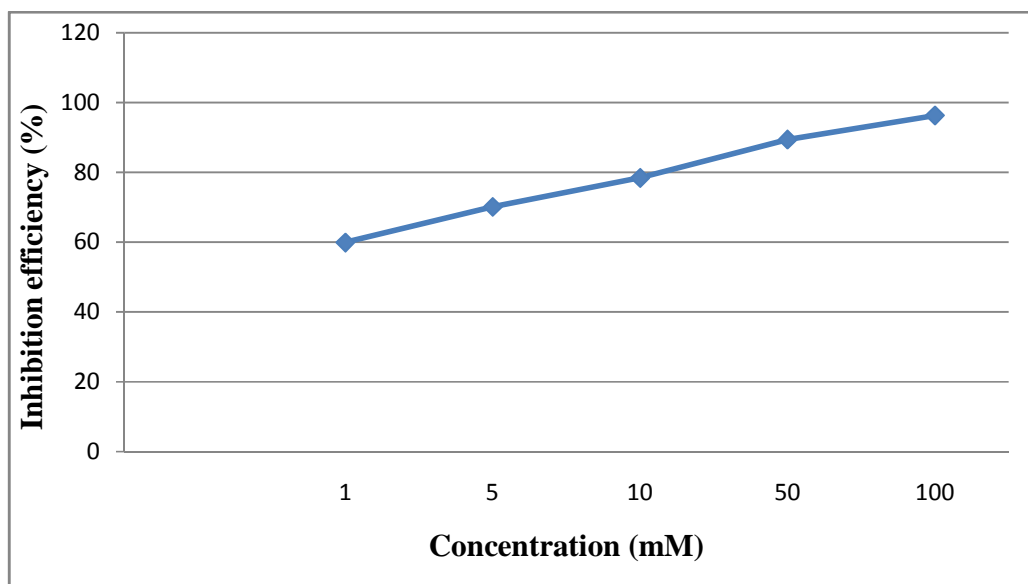
The value of percentage inhibition efficiency (% I E) and corrosion rate (CR) obtained from weight loss method at different concentrations of DES in 3M HNO₃ at 30°C are summarized in Table-1.

The variation of inhibition efficiency with increase in inhibitor concentrations is shown in Fig (2). It was observed that DES 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 HNO₃ at 30°C it is evident from table – 1 that the corrosion rate is decreased on the addition of DES.

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

Inhibitor	Concentration(mM)	% I. E	θ
Blank	3M HNO ₃	-	-
DES	1	60.0	0.60
	5	70.2	0.702
	10	78.5	0.785
	50	89.5	0.895
	100	96.4	0.964

Fig - 2 Variation of inhibition efficiency on Copper with different concentration of DES in 3M HNO₃ at 30°C for 2 hrs

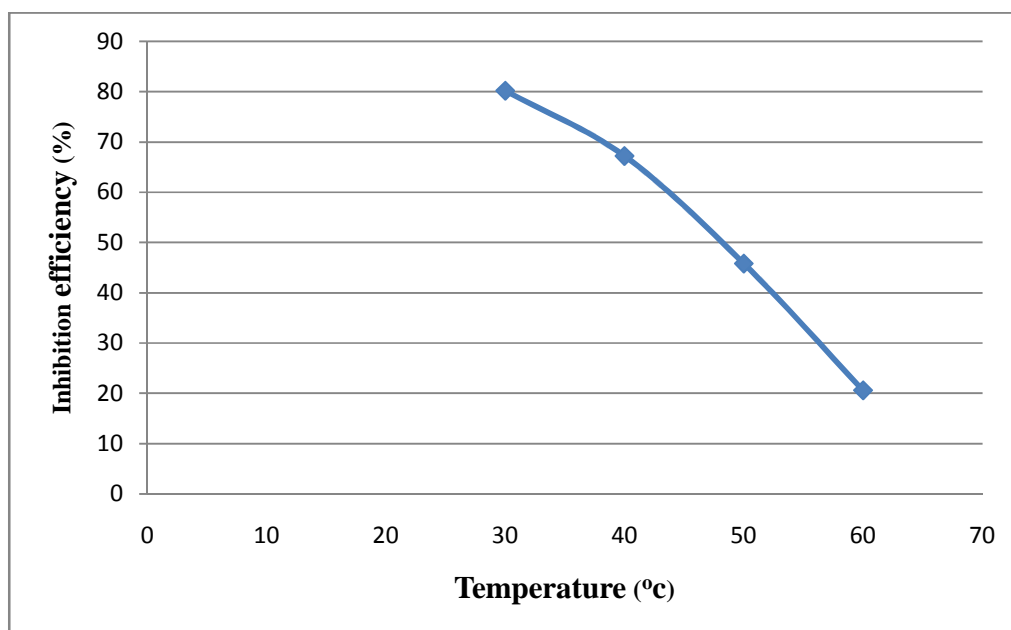


Temperatures Effects

The value of inhibition efficiency obtained from weight loss measurement at the different temperatures of 30°C to 60°C in 3M HNO₃ 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 3M HNO₃ in absence and presence of optimum concentration of DES at different temperature for 2 hrs

Temperature (°C)	Inhibitor	W (mg/cm ² .h)	% I. E
30	Blank	0.3932	-
	DES	0.0802	80.8
40	Blank	0.3124	-
	DES	0.0344	67.18
50	Blank	0.5723	-
	DES	0.0289	45.80
60	Blank	1.2031	-
	DES	0.0201	20.58

Fig - 3 Variation of inhibition efficiency on copper with different temperatures of DES in 3M HNO₃ for 2 hrs**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 inhibitor 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. % IE /100, where % IE is inhibition efficiency obtained by weight loss method. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitor on the copper surface.

The values of surface coverage (θ) for different concentration of inhibitor in 3M HNO₃ solution were evaluated from weight loss measurement. The inhibitor DES was 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 inhibitor suggesting that the adsorption isotherm relationship as shown in the fig (4) from this we can say that the inhibitor adsorption on it, is assumed that the adsorption of inhibitor at the metal solution interface is the first step in the action mechanism of inhibitor in aggressive acid medium [10-15].

Potentiodynamic polarization measurement

Current – potential characteristics resulting from cathodic and anodic polarization curves of copper in 3M HNO₃ in the presence and absence of DES at various concentrations are presented in Table – 3, gives values of corrosion current (I_{corr}), corrosion potential (E_{corr}) anodic and cathodic Tafel slop (b_a , b_c). In the case of polarization method the relation determines the inhibition efficiency (% I E)

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

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

Fig -4 Temkin's adsorption isotherm plots for copper in 3 M HNO₃ containing DES for 2 hrs

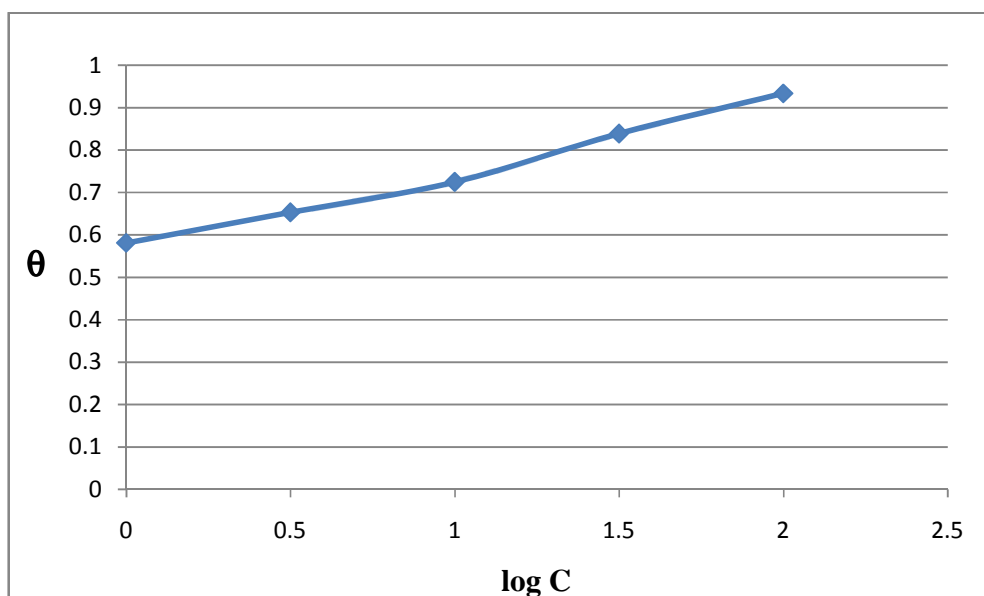
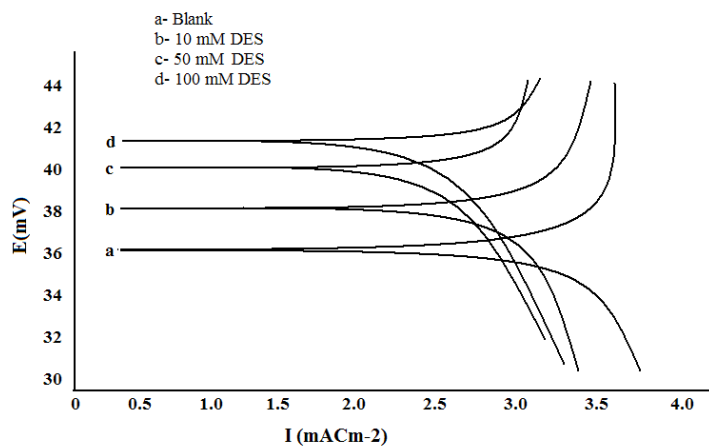


Table- 3 Corrosion kinetic parameters obtained from potentiodynamic polarization studies for copper in aqueous solution of 3M HNO₃ in absence and presence of different concentration of DES

Inhibitor	Concentration (mM)	E _{corr} mV Vs SCE	Tafel slops (mv/dec)		I _{corr} (mAcm ⁻²)	% I. E
			ba	-bc		
Blank	3 M HNO ₃	36	97	224	3.900	-
DES	10	38	103	197	2.705	46.5
	50	40	95	190	2.053	67.8
	100	41.5	90	187	1.903	90.7

Fig-5 Polarization obtained from potentiodynamic polarization studies for Copper in aqueous solution of 3 M HNO₃ in absence and presence of different concentration of DES



As it is shown in Tables - 3, and fig-5 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 DES more over a small effect is observed on the anodic portions. This result indicates that DES 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 DES acts as a mixed type inhibitor.

SEM analysis of metal surface

The SEM image of magnification (x 1000) of Copper specimen immersed in 3M HNO₃ for 2 hours in the absence and presence of inhibitor system are shown in fig.6 (b,c).

Fig-6 (a) Pure Copper metal

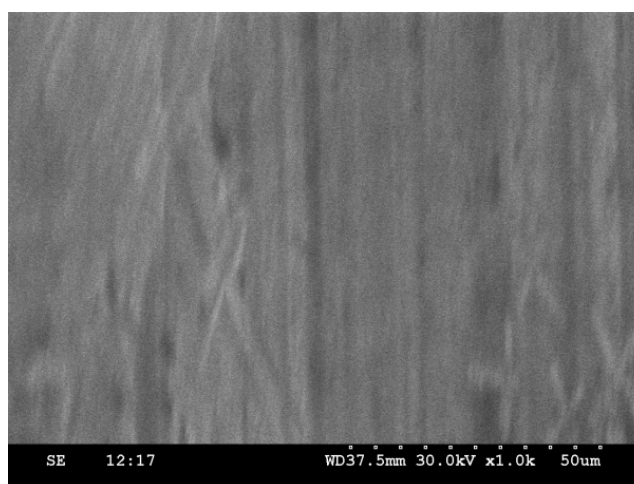


Fig-6 (b) Pure Copper metal + 3M HNO₃ Acid

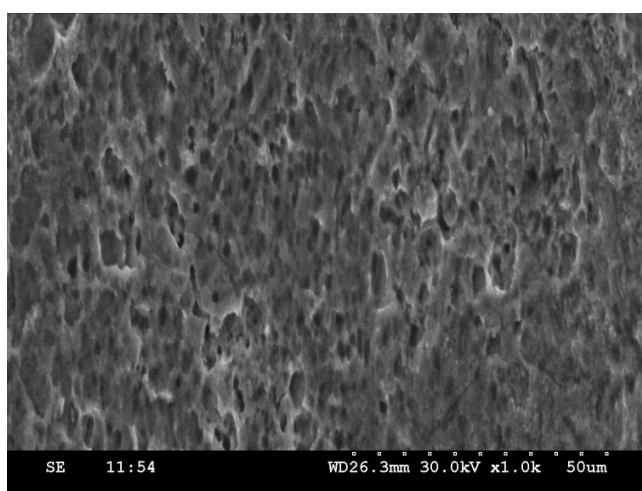
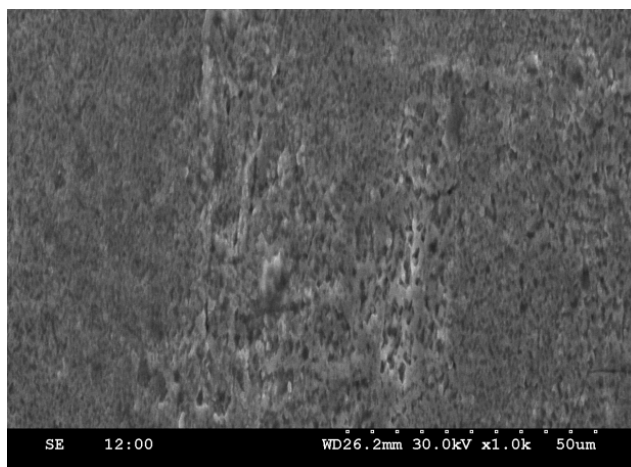


Fig-6 (c) Pure Copper metal + 3M HNO₃ Acid + Inhibitor (DES)

The SEM micrographs of polished copper surface (control) in fig.6 (a) the smooth surface of the metal. This shows the absence of any corrosion products formed on the metal surface.

The SEM micrographs of Copper surface immersed in 3M HNO₃ in fig.6 (b) Shows the roughness of the metal surface which indicates the corrosion of Copper in HNO₃. Fig.6(c) indicates that in the presence of 100 mM of DES, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal (DES inhibitor complex) and the surface is covered by a thin layer of inhibitor which effectively control the dissolution of Copper.

CONCLUSION

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

- Results obtained from the experimental data shown that DES 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 DES but decrease with rise in temperature
- The adsorption of DES on Copper surface from 3M HNO₃ obeys Temkin adsorption isotherm.
- Polarization measurements show that DES acts essentially as a mixed type inhibitor
- The SEM images confirm the formation of protective layer on the metal surface

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