Evaluation of corrosion inhibition of copper in nitric acid solutions using Organic sulphide compound

A. Jamal Abdul Nasser\(^1\) and V. Rethinagiri\(^2\)*

\(^1\)Department of Chemistry, Jamal Mohamed College, Trichy, India
\(^2\)Department of Chemistry, J J College of Engineering and Technology, Trichy, India

ABSTRACT

The inhibition of organic compounds containing a sulphur group such as Dipropylsulphide(DPS) 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 30-600\(^\circ\)C. 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 great 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 good alloy requiring strong oxidants for its corrosion. The chemical dissolution and electroplating 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 and 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 HNO\(_3\) 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 the Copper samples were mechanically polished using different grades of emery sheets, washed with trichloroethylene and triply distilled water and dried.
The organic compound used in this study was procured from Fluka AG, Switzerland, Analar grade HNO$_3$ was used for preparing the aggressive solution.

**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 HNO$_3$ 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.

\[
I \% = \frac{W_o - W_i}{W_o} \times 100
\]

Where

\(W_o = \text{weight loss in plain acid}\)
\(W_i = \text{weight loss in inhibited acid}\)

**Temperatures Effects**
The same procedure adopted for weight loss for studies at temperature of the study was varied from 30$^\circ$C to 60$^\circ$C 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 HNO$_3$ 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 (\(\theta\)) as a function of inhibitor concentration must be obtained. The values of \(\theta\) can be easily determined from the weight loss measurements by the ratio. \(\% \text{ I.E.} /100\), where \(\% \text{ I.E.}\) 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[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 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

**RESULTS AND DISCUSSION**
Molecular structure of organic compound used in the present study is given in

\[\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{S} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3\]

Fig 1: DiPropyl Sulphide(DPS)

**Weight loss measurements**
The value of percentage inhibition efficiency (\(\% \text{ I.E.}\)) and corrosion rate (CR) obtained from weight loss method at different concentrations of DPS in 3M HNO$_3$ at 30$^\circ$C.

The variation of inhibition efficiency with increase in inhibitor concentrations is shown in Fig (2). It was observed that DPS inhibits the corrosion of Copper in HNO$_3$ 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 30$^\circ$C it is evident from Fig (2) that the corrosion rate is decreased on the addition of DPS.
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 Fig 3. The inhibition efficiency decreased at high temperature.

Adsorption isotherm
The adsorption isotherm can be determined by assuming that inhibition effect is due mainly to the adsorption at metal/solution interface. Basic in 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 3MHNO₃ solution were evaluated from weight loss measurement. The inhibitor DPS 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].

![Fig-4: Temkin’s adsorption isotherm plots for Copper in 3M HNO₃ containing DPS for 2 hrs](image)

**Potentiodynamic polarization measurement**

Current – potential characteristics resulting from cathodic and anodic polarization curves of Copper in 3M HNO₃ in the presence and absence of DPS at various concentrations are presented in Table – 3, gives values of corrosion current (Iₑₙₑₓₚ), corrosion potential (Eₑₙₑₓₚ) anodic and cathodic Tafel slope (bₑ, bₓ). In the case of polarization method the relation determines the inhibition efficiency (% Iₑ) where $Iₑₙₑₓₚ$ and $Iₑₙₑₓₚ$ are the uninhibited and inhibited corrosion current densities.

$$\% \text{ Iₑ} = \left(1 - \frac{Iₑₙₑₓₚ}{Iₑₙₑₓₚ}\right) \times 100$$

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 DPS.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration (mM)</th>
<th>$Eₑₙₑₓₚ$ (mV vs. HRE)</th>
<th>Tafel slopes (mv/dec)</th>
<th>$Iₑₙₑₓₚ$ (mA/cm²)</th>
<th>% Iₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3 M HNO₃</td>
<td>21</td>
<td>45.86-2968</td>
<td>3.666</td>
<td>-</td>
</tr>
<tr>
<td>DPS</td>
<td>100</td>
<td>43</td>
<td>95-187</td>
<td>1.899</td>
<td>91.7</td>
</tr>
</tbody>
</table>

As it is shows in Tables - 3, cathodic current – potential curves give rise to parallel Tafel lines indicating that the cathodic current density decreases with the concentration of DPS more over a small effect is observed on the anodic portions. This result indicates that DPS 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 DPS 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.5 (a, b).
The SEM micrographs of Copper surface immersed in 3M HNO$_3$ in fig. 5 (a) shows the roughness of the metal surface which indicates the corrosion of Copper in HNO$_3$. Fig. 5(b) indicates that in the presence of 100 mM of DPS, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal (DPS inhibitor complex) and the surface is covered by a thin layer of inhibitor which effectively control the dissolution of Copper.

**SEM Images**

![SEM Image of Pure Copper + 3M HNO$_3$ Acid](image1)

![SEM Image of Pure Copper + 3M HNO$_3$ Acid + Inhibitor (DPS)](image2)

**CONCLUSION**

On the basis of the above results the following conclusion can be drawn.
- Results obtained from the experimental date shown that DPS 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 DPS but decrease with rise in temperature.
- The adsorption of DPS on Copper surface from 3M HNO$_3$ obeys Temkin adsorption isotherm.
- Polarization measurements show that DPS acts essentially as a mixed type inhibitor.
• The SEM images confirm the formation of protective layer on the metal surface

Acknowledgement

Corresponding author (V.RethinaGiri) wish to thank ful to the university grants commission, India and the Chairman, J.J. College of Engineering and Technology, Trichy-09 for his cooperation and encouragement.

REFERENCES