

## CORROSION BEHAVIOUR OF COPPER IN SULPHURIC ACID IN THE PRESENCE OF N-METHYLANILINE

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### Abstract

*In this paper, the corrosion behaviour of copper in sulphuric acid solution and in the presence of N-methylaniline (MA) was investigated. The inhibitory effect of MA has been studied by several methods, i.e., weight loss measurements, linear polarization, Tafel plots method for kinetic parameters determination and scanning electron microscopy, all of them providing complete information about the inhibition mechanism.*

**Keywords:** N-methylaniline, copper corrosion, corrosion inhibitor, inhibitor efficiency

### INTRODUCTION

Metallic copper has a wide range of industrial applications due to its relatively low cost and superior properties. Usually, copper is used as a material in heating and cooling systems (Khaled K.F., 2008, Simonovic A. T. et al, 2014, Stupnisek-Lisac E. et al, 2002) owing to its excellent thermal conductivity, good malleability and easy machining. Among the possible uses of the copper in electrochemical processes the galvanic depositions, either as a final layer used in electrical and electronic applications can be mentioned (Cho C. H. et al, 2013, Tumkin I. I. et al, 2015), or as an intermediate layer for depositing other metals due to its good adhesion (Somasundaram S. et al, 2015, Liu X. et al, 2013). During the last period, new uses for electrochemical applications (Ngamlerdpokina K. et al, 2014, Văduva C.C. et al, 2011, Jakab A. et al, 2015) of metallic copper have been found. Even if it shows a considerable resistance towards different chemical reagents action, copper may corrode in certain environments.

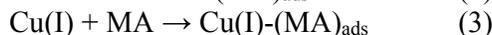
The use of inhibitors is one of the most effective methods for combating copper corrosion, especially in aggressive liquids. Recently, the goal of much research was the copper corrosion prevention, so until now numerous types of inhibitors have been investigated. Amongst them there are inorganic inhibitors, but mainly organic compounds and their derivatives have been studied such as azoles, amines, amino acids and many others (Khaled K.F., 2008).

The pH value of the solution and the reaction medium has a considerable influence both on the inhibitor and also the corrosion

behaviour of copper electrode. It is well-known that in strongly acid solutions amines exist in a protonated form according to the equilibrium (Jakab A. et al, 2015):



M. M. Antonijevic and M. B. Petrovic have studied the possibility of using various amines as copper corrosion inhibitors. According to their interpretation, in the presence of N-methylaniline (MA) in strong acid medium the following reactions with protective role for copper metallic against corrosion attack occur (Antonijevic M. M. et al, 2008):



Despite the fact that MA acts as catalyst for hydrogen evolution reaction, it blocks the anode areas on which metallic copper ionization occurs.

In this study, the MA influence on corrosion inhibition efficiency of copper in sulfuric acid solutions was studied using both electrochemical and gravimetric methods.

## MATERIAL AND METHOD

### Materials

In order to study the corrosion behaviour of copper in 0.5 M H<sub>2</sub>SO<sub>4</sub> and the inhibitor effect of MA, different concentrations of organic compounds (10<sup>-6</sup> ÷ 10<sup>-3</sup> M) have been used. The chemicals used for this study *i.e.*, sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and N-methylaniline (MA, analytical grade) were purchased from Merck Company (Germany). The chemical structure of MA (C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>) is presented in figure 1. The corrosion test electrode was a cylindrical disc cut from a copper electrolytic sample.

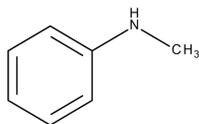


Fig.1 Chemical structure of N-methylaniline.

### Methods

Cyclic voltammetry, linear polarization and weight loss methods were used in order to notice the inhibitive properties of MA on copper corrosion process in acid solutions. The surface morphology of copper samples has been characterized by scanning electron microscopy (SEM) using a FEI INSPECT S microscope. The experimental set-up consisted of a conventional three-electrode 100 mL glass cell and a Biologic SP150

potentiostat/galvanostat. The potentiostat was connected with two graphite counter electrodes, Ag/AgCl reference electrode and a copper working electrode with 1 cm<sup>2</sup> surface area. The working electrode surface was polished before each experiment with different grit abrasive paper, cleaned in ultrasonic bath and rinsed with distilled water. The electrode potential was allowed to stabilize 60 minutes before each measurement.

## RESULTS AND DISCUSSION

### *Cyclic voltammetry method*

In order to obtain information concerning MA electrochemical oxidation/reduction behaviour as well as how the organic compound influences cathodic and/or anodic processes, voltammetric tests were performed on Pt electrode. In figure 2a ( $dE/dt = 500 \text{ mV s}^{-1}$ ) and b ( $dE/dt = 10 \text{ mV s}^{-1}$ ) are presented the cyclic voltammograms recorded on Pt electrode, in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions without and with 10<sup>-3</sup> M MA.

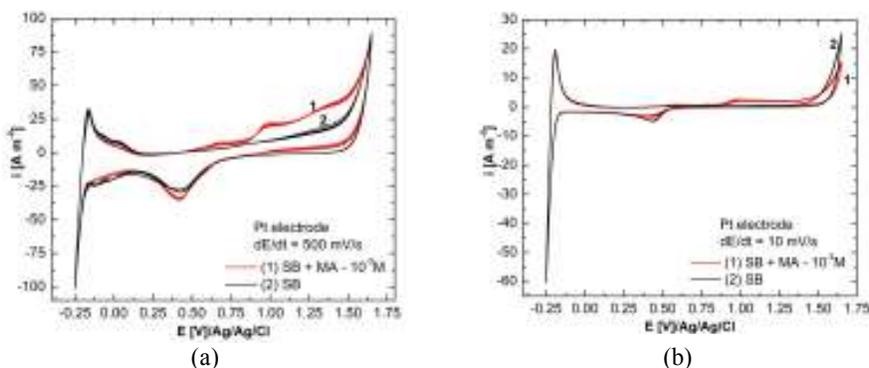


Fig.2 Cyclic voltammograms (5 cycles) on Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence/presence of 10<sup>-3</sup> M MA, scan rate: (a) - 500 mV s<sup>-1</sup>, (b) - 10 mV s<sup>-1</sup>.

The background curve recorded in blank solution is one characteristic polarization curve drawn in H<sub>2</sub>SO<sub>4</sub> solutions. On the anodic branch, only the plateau corresponding to evolution of oxygen can be observed. On the backward scan, a new cathodic peak appears at about +0.4V vs. Ag/AgCl, that can be associated with the oxidation of superficial oxides and also at more negative potentials (-0.2 V) the hydrogen evolution can be observed. The addition of organic compound in the blank solution leads to a visible increase of the current that can be attributed to the MA oxidation recorded between +0.5 and +1.4 V vs. Ag/AgCl. The amine oxidation could lead to an attachment of the organic group to the Pt surface, and it was proposed that the nitrogen was bonded to the metal surface, as shown in the following reaction (Adenier A. et al, 2004):



The oxidation mechanism of amines consists in 5 steps with different rates, as can be observed in figure 2a (Adenier A. et al, 2004). The applied potential corresponding to the oxidation of organic compound is not significant for the copper corrosion process, which takes place at much negative potential values, as will be seen in experimental data presented below.

Cyclic voltammograms drawn on copper electrode in the same electrolyte solution with and without addition of MA are presented in figure 3a; in the cathodic domain polarization curves were recorded separately and are shown in figure 3b.

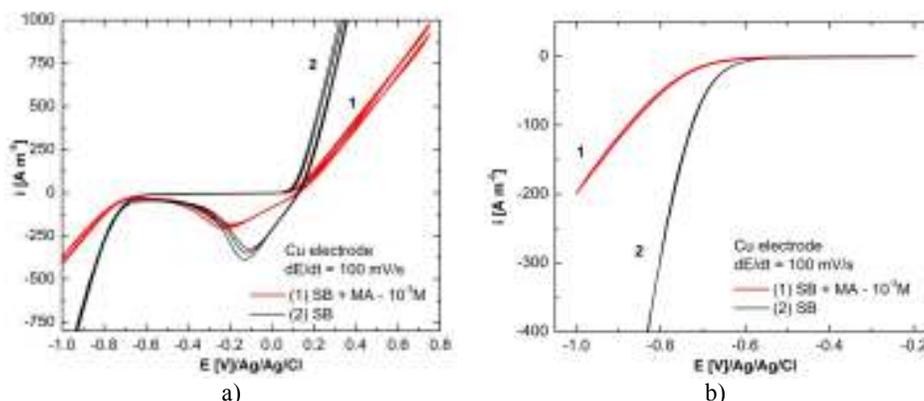


Fig.3 Cyclic voltammograms (3 cycles) on copper electrode in 0.5 M  $\text{H}_2\text{SO}_4$  in the absence/presence of  $10^{-3}$  M MA, scan rate:  $100 \text{ mV s}^{-1}$ : (a) cathodic-anodic domain and (b) cathodic polarization

As one can see, the cathodic curves are shifted to more negative potential values and the hydrogen evolution reaction is inhibited in the presence of MA; a similar behaviour can be observed for anodic oxygen evolution reaction on copper electrode.

#### *Linear polarization method*

The MA effect on copper corrosion process was studied in 0.5 M  $\text{H}_2\text{SO}_4$  corrosive environments by applying successive investigations presented above. Experimental measurements were carried out after 1 h, considered sufficient time to install an electrode equilibrium or quasi-equilibrium state, as shown in figure 4. In table 1 open circuit potential values after 1 hour immersed time in test solution are presented.

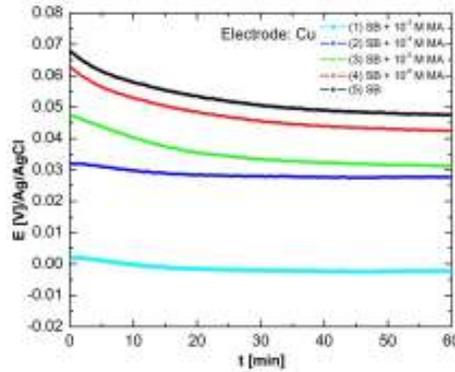


Fig.4 OCP for copper electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> and in the presence of different concentrations of MA, at 293 K.

In the presence of different concentrations of MA, the electrode potential is shifted to more negative values, phenomenon that can be attributed to the adsorption of organic molecules on the electrode surface.

Table 1

Copper electrode  $E_{OCP}$  values in blank solutions

Electrode	Electrolyte [M]	Temperature [K]	$E_{OCP}$ [mV]
Cu	Blank	293	47.6
	Blank + 10 <sup>-6</sup> MA		42.4
	Blank + 10 <sup>-5</sup> MA		30.7
	Blank + 10 <sup>-4</sup> MA		27.9
	Blank + 10 <sup>-3</sup> MA		-2.15

The manner in which MA acts as corrosion inhibitor for copper in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and how its effect the corrosion rate can be estimated by different procedures, one of the most used method being the Tafel polarization method. The potentiodynamic polarization curves recorded without and with various concentrations of MA are shown in figure 5.

The numerical values of the variation of the corrosion current density ( $i_{corr}$ ), the corrosion potential ( $E_{cor}$ ), the anodic Tafel slope ( $b_a$ ) and the cathodic Tafel slope ( $b_c$ ), the polarization resistance ( $R_p$ ), with various concentrations of inhibitor were obtained from polarization profiles by extrapolating potentiodynamic curves using BioLogics software. The inhibition efficiency ( $IE$ ) has been calculated using equations (5) and the obtained values are gathered in Table 2.

$$IE(\%) = \left( \frac{i_{corr}^0 - i_{corr}^{inh}}{i_{corr}^0} \right) \times 100 \quad (5)$$

where  $i_{corr}^0$  and  $i_{corr}^{inh}$  are the uninhibited and inhibited corrosion current densities, respectively.

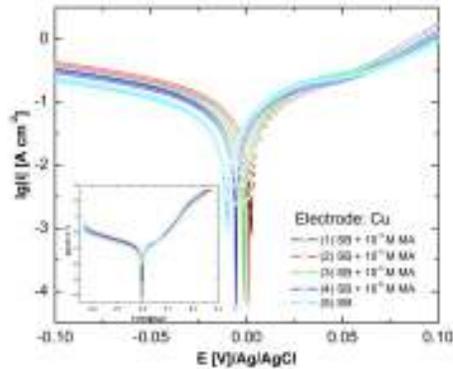


Fig.5. Linear polarization diagrams on copper electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence/presence of MA, at 293 K, scan rate: 1 mV s<sup>-1</sup>.

The Tafel curves presented in figure 5 show that MA has a significant influence for both cathodic hydrogen evolution reaction and anodic dissolution/passivation of the metal.

Table 2

Copper corrosion polarization parameters:

MA conc. [M]	Temp. [K]	$i_{cor}$ [ $\mu\text{A cm}^{-2}$ ]	$E_{cor}$ [mV]	$-b_c$ [mV dec <sup>-1</sup> ]	$b_a$ [mV dec <sup>-1</sup> ]	$R_p$ [ $\Omega$ ]	$v_{cor}$ [mm an <sup>-1</sup> ]	$IE$ [%]
Blank	298	7.84	2.01	201	64.5	2440	0.36	-
10 <sup>-6</sup>		6.58	0.68	206	66.9	3470	0.32	16.1
10 <sup>-5</sup>		5.94	-1.99	210	69.4	3610	0.28	24.2
10 <sup>-4</sup>		5.23	-5.93	218	72.1	4460	0.25	33.3
10 <sup>-3</sup>		4.18	-9.91	225	74.9	5110	0.20	46.7

The obtained results reveal that the corrosion rate decreases and hence inhibition efficiency ( $IE$ ) increases as the concentration increases. In addition, the highest inhibition efficiency has been obtained for 10<sup>-3</sup> M MA at 298 K.

#### Weight loss method

Gravimetric measurements were investigated after 240 hours immersion time at room temperature, the copper disc samples were immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with different amounts of MA, in order to compare the inhibition efficiencies at the selected concentrations. As it was expected the weight loss of copper samples are decreased with the increase of amine concentrations, meaning that MA act as inhibitor. The corrosion rate of copper ( $W_L$ ) was determined using the relation (6) and the inhibition efficiency ( $IE$ ) calculated by equation (7):

$$W_{corr} = \left( \frac{W_1 - W_2}{S \times t} \right) \times 100 \quad (6)$$

where  $W_1$  and  $W_2$  are the initial and final mass of the samples in mg,  $S$  is total surface area in  $\text{cm}^2$  and  $t$  is exposure time in h.

$$IE(\%) = \left(1 - \frac{W_{corr}}{W_{corr}^0}\right) \times 100 \quad (7)$$

where  $W_{corr}$  and  $W_{corr}^0$  are the weight loss in the presence and the absence of inhibitor, respectively.

Table 3

The inhibition efficiencies obtained by weight loss method:

Electrolyte [M]	$W_L$ [ $\text{mg cm}^{-2} \text{h}^{-1}$ ]	$E$ [%]
Blank	0.052	-
Blank + $10^{-6}$ MA	0.045	14.9
Blank + $10^{-5}$ MA	0.039	25.2
Blank + $10^{-4}$ MA	0.030	33.9
Blank + $10^{-3}$ MA	0.022	45.1

#### Surface analysis

SEM analysis was performed to analyze the surface morphology of copper samples after 240 h immersion time in 0.5 M  $\text{H}_2\text{SO}_4$  in the absence (Fig.7a) and in the presence of  $10^{-3}$  M MA (Fig.7b) at room temperature. In the absence of inhibitor, damaged surface was observed due to the high dissolution rate of copper in sulphuric acid solution.

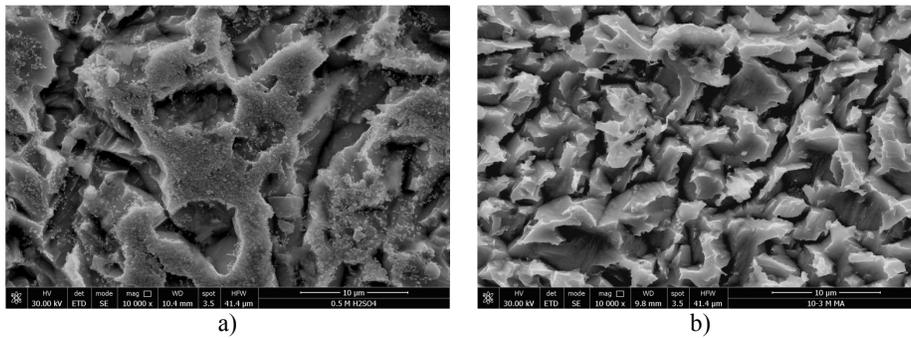


Fig.7 SEM images obtained for copper after 10 days immersion time in 0.5M  $\text{H}_2\text{SO}_4$  without (a) and with  $10^{-3}$  M MA (b).

## CONCLUSIONS

Inhibition effect of MA has been studied by two different methods: weight loss and linear polarization, both giving comparable results. MA exhibited good inhibition performance as a mixed-type inhibitor for copper electrode in 0.5 M  $\text{H}_2\text{SO}_4$ . The maximum inhibition efficiency of MA for

copper corrosion in acid solution was 47%. SEM micrographs showed that the inhibitor molecules form a protective film on the copper surface.

#### ACKNOWLEDGEMENTS

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