

# Inhibitory Properties of N,N-dimethylaniline for Copper in Sulphuric Acid Solutions

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**Abstract:** In this study, the inhibitive action of N,N-dimethylaniline (DMA) on copper corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different temperatures was investigated using linear polarization and weight loss methods. The electrochemical behaviour of DMA on platinum and copper electrodes in acid solutions has been analyzed by cyclic voltammetry. Inhibitory properties of DMA for copper corrosion protection were studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions in the presence of different concentrations of inhibitor 10<sup>-6</sup> M, 10<sup>-5</sup> M, 10<sup>-4</sup> M and 10<sup>-3</sup> M, respectively. The morphology of copper samples obtained in the absence and presence of DMA has been studied by scanning electron microscopy (SEM). The obtained results showed that DMA is an anodic type inhibitor for copper corrosion in sulphuric acid solutions.

**Keywords:** N,N-dimethylaniline, corrosion inhibitor, copper corrosion, inhibition efficiency

## 1. Introduction

The use of inhibitors is one of the most adequate means to mitigate or eliminate the undesirable effects of corrosion processes, due to the advantages, *i.e.*, possibility to be used in equipment already in operation, relatively easy introduction in corrosive environment and ability to form protective layer on the exposed metal surfaces. A large number of substances with inhibitory effect on corrosion processes allow finding suitable solutions for many problems caused by corrosion, but certainly not for all cases occurring in practice. Although, the use of inhibitors is a convenient and effective method for corrosion protection, the selection of the appropriate product for a given corrosion environment must be made discerning. Also inhibitors should have high persistence and a molecular structure that allow strong adsorption on the metal surface in order to resist to the corrosive effect of the fluid flowing.

The possibility of copper corrosion prevention using mostly organic inhibitors has attracted many researchers. The most widely used inhibitors are organic compounds derivatives such as azoles [1,2], amines [3,4], amino acids [5] and many others. Ehteshamzade et al. [6] studied the inhibitive action of Schiff bases N,N'-ethylenbis(salicylideneimine) (S-E-S) and N,N'-ortho-phenylenbis(salicylideneimine) (S-o-ph-S) self-assembled films on copper surface in 0.88 M NaCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions. It was found that S-o-ph-S is more efficient than S-E-S. When the concentration is increased the inhibition efficiency increases but that kind of application is not economical in industrial conditions. The presence of nitrogen heteroatoms in organic compounds like amines improves its action as copper corrosion inhibitor [7].

The aim of this study was to investigate the inhibitory effect of N,N-dimethylaniline (DMA) in 0.5 M H<sub>2</sub>SO<sub>4</sub> on

copper at different temperatures using linear polarization, cyclic voltammetry, scanning electron microscopy and weight loss measurements. The obtained results are useful in those cases when copper is used as the electrode in sulfuric acid solutions, *e.g.*, electrochemical deposition of copper in which DMA acts as levelling agent.

## 2. Experimental

The chemicals used for this study *i.e.*, sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and N,N-dimethylaniline (DMA, (CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>5</sub>) (analytical grade) were purchased from Merck Company (Germany). The distilled water was used for all experiments. Inhibitory properties of DMA for copper corrosion protection were studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions in the presence of different concentrations of inhibitor 10<sup>-6</sup> M, 10<sup>-5</sup> M, 10<sup>-4</sup> M, 10<sup>-3</sup> M. Direct and indirect methods were carried out to observe the inhibition effect of metal corrosion process, *i.e.*, cyclic voltammetry, gravimetric method, linear polarization method (Tafel curves) and scanning electron microscopy (SEM). The experimental set-up consisted of a conventional three-electrode single-chamber 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 0.5 cm<sup>2</sup> surface area. The working electrode surface was polished before each experiment with a soft abrasive paper and rinsed with distilled water. Weight loss ( $W_L$ ) experiments were carried out using disc samples of copper, before and after the corrosive attack in the presence and absence of different amounts of DMA they have been weighed. By measuring the loss of weight of the materials as a function of time the corrosion rate can be calculated using Eq(1):

$$W_L = \frac{m_i - m_f}{S \times t} \quad (1)$$

where  $W_L$  the weight loss in  $\text{mg cm}^{-2} \text{ h}^{-1}$ ;  $m_i$ ,  $m_f$  are the initial and final mass of the samples in mg;  $S$  is the total surface area in  $\text{cm}^2$  and  $t$  is the exposure time in h. Also, from the calculated  $W_L$  the inhibition efficiency ( $IE\%$ ) was obtained using Eq(2):

$$IE(\%) = (1 - W_L^{\text{inh}}/W_L^0) \times 100 \quad (2)$$

where  $W_L^{\text{inh}}$ ,  $W_L^0$  are the weight loss of the samples in the presence and absence of the inhibitor, respectively.

### 3. Results And Discussion

#### 3.1. Cyclic voltammetry measurements

In order to obtain more information about DMA oxidation/reduction resistance, as well as about its influence on cathodic and/or anodic processes, voltammetric measurements were carried out first on Pt electrode and further on metallic copper. Figure 1 shows cyclic voltammograms recorded on Pt in 0.5 M  $\text{H}_2\text{SO}_4$ , in the presence of  $10^{-3}$  M DMA, at  $500 \text{ mV s}^{-1}$ . On the background curve recorded in acid medium occur characteristic peaks corresponding to the oxidation of hydrogen adsorbed on the electrode surface ( $-0.20 \text{ V}$ ), evolution of oxygen at high positive potentials ( $+1.62 \text{ V}$ ) and hydrogen evolution at more negative potentials ( $-0.25 \text{ V}$ ).

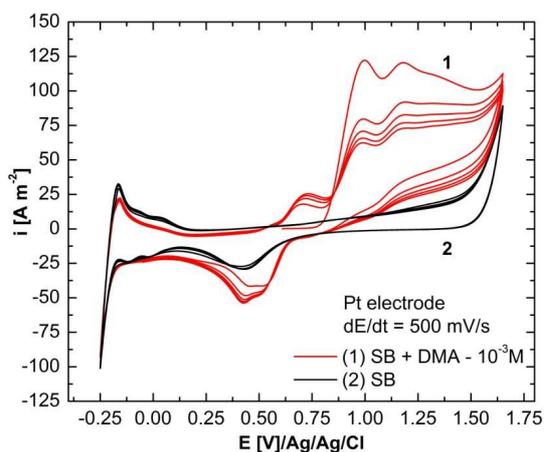


Figure 1. Cyclic voltammograms recorded on Pt electrode in 0.5 M  $\text{H}_2\text{SO}_4$  (2) and in the presence of  $10^{-3}$  M DMA (1), scan rate:  $500 \text{ mV s}^{-1}$

In the absence of inhibitor, the plateau between  $+0.8 \text{ V}$  and  $+1.25 \text{ V vs. Ag/AgCl}$  is less obvious due to the reduced sensitivity of the current axis, that can be associated with the formation of superficial oxides on the electrode surface, which are reduced on the reverse run at about  $+0.5 \text{ V vs. Ag/AgCl}$ . The addition of inhibitor in the blank solution leads to an increase of the current that can be attributed to

DMA oxidation. Earlier studies reported [8], the major product from DMA oxidation in aqueous solutions was the 4-4' (C-C) coupled compound  $N,N,N',N'$ -tetramethylbenzidine (THB), that being more easily oxidized than DMA and forms a stable dication. Moreover, in strongly acid solutions, DMA exists as protonated form,  $\text{DMAH}^+$ , that is electrochemically inactive. The cyclic voltammograms recorded on Pt in 0.5 M  $\text{H}_2\text{SO}_4$  and in the presence of  $10^{-3}$  M DMA at different polarization rates are presented in Figure 2.

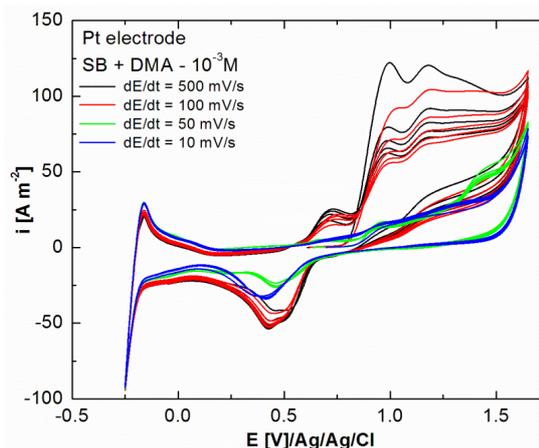


Figure 2. Cyclic voltammograms recorded on Pt in 0.5 M  $\text{H}_2\text{SO}_4$  and in the presence of  $10^{-3}$  M DMA at different polarization rates

Cathodic and anodic polarization curves were drawn on Pt electrode in blank solution and in the presence of  $10^{-3}$  M DMA at different scan rates to highlight the electrochemical behaviour of the inhibitor and the way how it can affect the electrode processes. In Figure 3a,b two such examples for cathodic and anodic cyclic voltammograms are presented.

Adding DMA in blank solution leads to the appearance of obvious peak corresponding to the inhibitor oxidation process recorded at about  $+0.9 \text{ V vs. Ag/AgCl}$ . Also, the anodic oxidation process takes place in two successive stages appearing two current plateau, the first between  $+0.9 \text{ V} \div +1.25 \text{ V vs. Ag/AgCl}$  and the second between  $+1.25 \text{ V} \div +1.5 \text{ V vs. Ag/AgCl}$ .

According to the above-presented cyclic voltammograms (Figure 3a,b), it can be observed that the presence of inhibitor does not influence significantly the cathodic hydrogen evolution, but it has a pronounced influence on the anodic oxygen evolution process, probable due to the adsorption of the inhibitor molecules on Pt electrode surface. Figure 4 show the cyclic voltammograms recorded on copper electrode in blank solution in the absence and presence of  $10^{-3}$  M DMA at  $100 \text{ mV s}^{-1}$ .

In the solution without inhibitor, by sweeping the potential from the open circuit potential to anodic direction, only the oxidation of metallic copper is observed, which concomitantly occurs with the hydrogen evolution process on copper electrode surface. On the reverse run a reduction peak appears at about  $-0.1 \text{ V vs. Ag/AgCl}$ , attributed to the reduction of adsorbed oxygen on copper surface or the reduction of copper ions formed in the oxidation step.

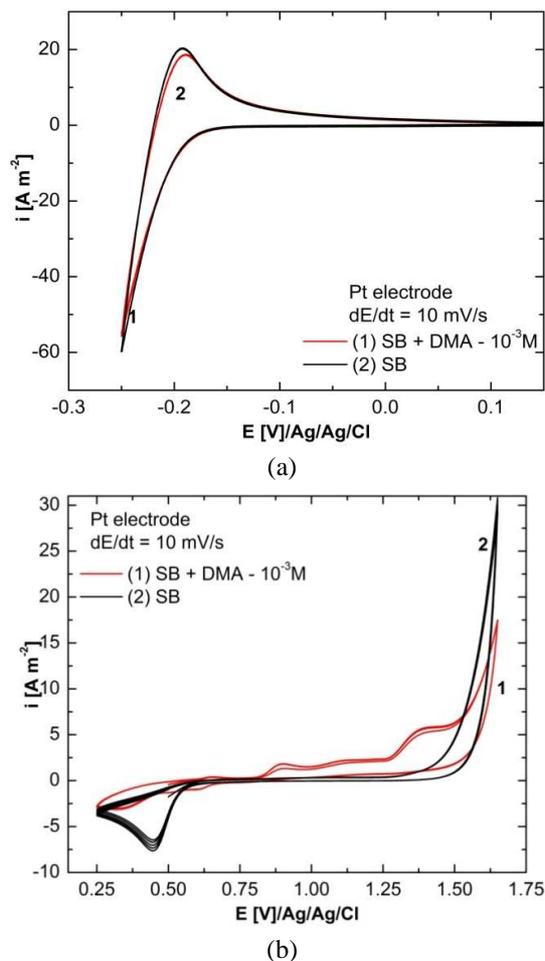


Figure 3. Cyclic voltammograms recorded for cathodic (a) and anodic (b) branch on Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> and in the presence of 10<sup>-3</sup> M DMA, scan rate: 10 mV s<sup>-1</sup>.

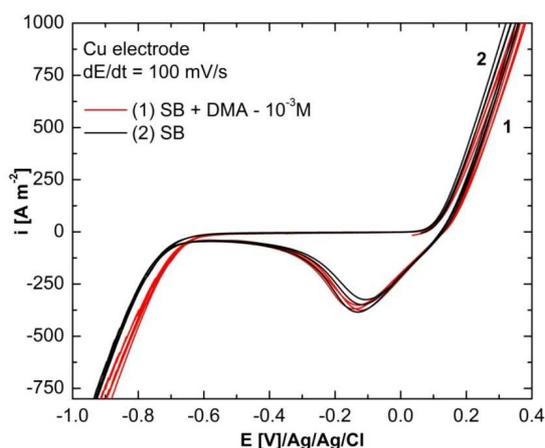


Figure 4. Cyclic voltammograms recorded on copper electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> (2) and in the presence of 10<sup>-3</sup> M DMA (1), scan rate 100 mV s<sup>-1</sup>.

The current peak corresponding to the copper ions reduction to metallic copper was recorded only at high scan rates, after scanning to anodic direction, since in this case the metal ions do not have time to diffuse in the solution

mass. Further, hydrogen evolution takes place at the applied potential values lower than -0.6 V vs. Ag/AgCl.

To obtain more information about the influence of DMA on copper corrosion process, especially in cathodic branch, cyclic voltammograms were recorded at a narrow potential range, which are presented in Figure 5.

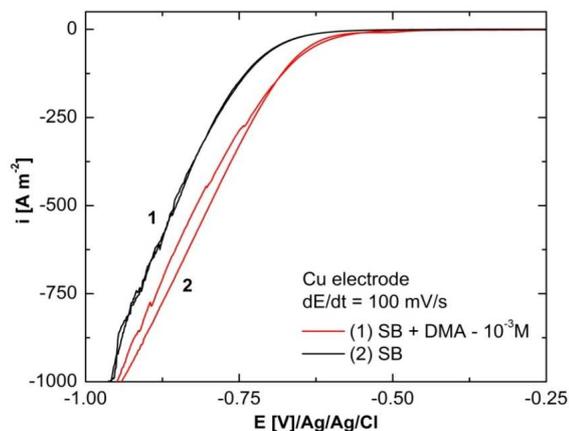


Figure 5. Cyclic voltammograms on copper electrode recorded in cathodic branch in 0.5 M H<sub>2</sub>SO<sub>4</sub> (2) and in the presence of 10<sup>-3</sup> M DMA (1) with 100 mV s<sup>-1</sup> scan rate.

In the presence of DMA, at negative potentials the hydrogen evolution can be observed, as well as a shift of the applied anodic potential in the positive direction, in accordance with the obtained results which have been reported in our previous published paper [9].

### 3.2. Effect of DMA concentration

Tafel polarization curves were recorded on copper electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> and in the presence of different concentrations of DMA at 2 mV s<sup>-1</sup>, which are presented in Figure 6. The voltammograms were recorded in deoxygenated solutions to avoid side effect that may occur on the electrode surface after reaching equilibrium of the electrode in the electrolyte solution.

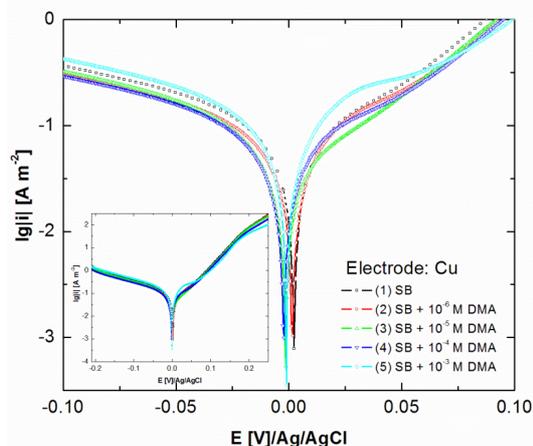


Figure 6. Tafel polarization diagrams recorded on Cu ( $dE/dt = 2 \text{ mV s}^{-1}$ ) in 0.5 M H<sub>2</sub>SO<sub>4</sub> and in the presence of different concentrations of DMA

Polarization parameters for the corrosion of copper, i.e., corrosion potential ( $E_{cor}$ ), corrosion current density ( $i_{cor}$ ), cathodic and anodic Tafel slopes ( $b_c$  and  $b_a$ ), polarization resistance ( $R_p$ ) and corrosion rate ( $v_{cor}$ ) were determined by extrapolating potentiodynamic curves. The inhibition efficiency  $IE(\%)$  and surface coverage ( $\theta$ ) have been calculated with Eq(3) and Eq(4) and the obtained results are gathered in Table 1.

$$IE(\%) = ((i_{cor}^o - i_{cor}^{inh}) / i_{cor}^o) \times 100 \quad (3)$$

$$\theta = (i_{cor}^o - i_{cor}^{inh}) / i_{cor}^o \quad (4)$$

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

TABLE 1. Polarization parameters for the corrosion of copper in 0.5 M  $H_2SO_4$  presence/absence different concentrations of DMA at 298 K.

Inh. con., M	$i_{cor}$ , $\mu A/cm^2$	$E_{cor}$ , mV	$-b_c$ , mV/dec	$b_a$ , mV/dec	$R_p$ , $\Omega$	$v_{cor}$ , mm/an	$IE$ , %	$\theta$
BS	7.84	2.01	221	64.5	2440	0.36	-	-
$10^{-6}$	5.23	1.25	225	70.8	3510	0.24	33.3	0.33
$10^{-5}$	5.11	-1.49	218	72.6	3820	0.23	34.8	0.35
$10^{-4}$	5.01	-3.28	210	75.0	4230	0.23	36.1	0.36
$10^{-3}$	4.75	-5.04	205	82.5	4760	0.21	39.4	0.39

Based on the above-presented results, it can be noticed that DMA act as anodic type of inhibitor. In addition, Tafel slopes do not suffer significant modifications in the presence of inhibitor, suggesting that the presence of DMA does not modify the overall mechanism of copper corrosion process. The addition of different concentrations of inhibitor leads to increase the number of DMA molecules on the copper-electrolyte interface and decreasing the corrosion current densities by shifting the corrosion potential values slightly in the more negative direction. DMA is protonated in sulphuric acid forming aryl-ammonium ions [10], which are preferentially oriented with the ammonium group to the metal surface and the inhibition effect is due to their strong adsorption on the active corrosion sites or the deposition of corrosion products on the copper surface [11].

### 3.3. Effect of temperature

The influence of temperature on copper corrosion process was studied by polarization method, the Tafel slopes are given in Figure 7. The effect of temperature on copper corrosion in 0.5 M  $H_2SO_4$  and in the presence of  $10^{-3}$  M DMA was investigated at 298, 308, 318, 328 and 338 K, and the obtained results are gathered in Table 2.

In the presence of inhibitor, it can be observed an increase of copper corrosion rate with temperature increasing, from 0.21 at 298 K to 0.37 mm an<sup>-1</sup> at 328 K. It is obviously that inhibitory effect of DMA is not favoured by increasing temperature, according to the comparison of

the corrosion potential values  $E_{cor}$ , -5.0 mV vs. Ag/AgCl at 298 K and +31.0 mV vs. Ag/AgCl at 328 K.

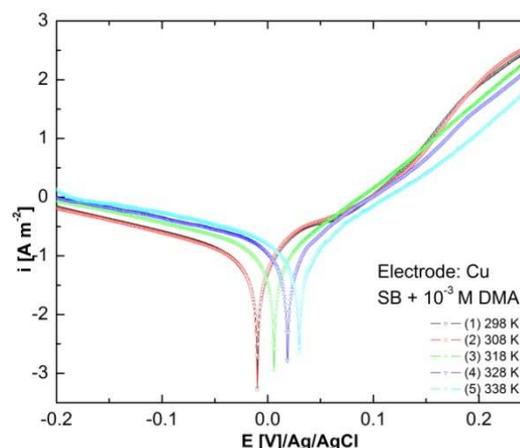


Figure 7. Tafel polarization diagrams recorded on Cu ( $dE/dt = 2 \text{ mV s}^{-1}$ ) in 0.5 M  $H_2SO_4$  and in the presence of  $10^{-3}$  M DMA at different temperatures.

TABLE 2. Polarization parameters for copper corrosion in 0.5 M  $H_2SO_4$  and in the presence of  $10^{-3}$  M DMA at different temperatures.

T, K	$i_{cor}$ , $\mu A/cm$	$E_{cor}$ , mV	$-b_c$ , mV/dec	$b_a$ , mV/dec	$R_p$ , $\Omega$	$v_{cor}$ , mm/an
298	4.75	-5.0	205	82.5	4760	0.21
308	4.61	-0.4	190	71.4	3720	0.22
318	3.89	6.1	109	69.6	2920	0.25
328	3.06	19.2	90	67.2	2420	0.31
338	2.15	31.0	70	65.4	2240	0.37

### 3.4. Weight loss data

Gravimetric method was used to obtain weight loss data and inhibition efficiencies of copper samples after 240 hour immersion time in 0.5 M  $H_2SO_4$  solutions and in the presence of different amounts of DMA, the obtained results are given in Table 3.

TABLE 3. Inhibition efficiencies obtained by weight loss measurements

DMA, M	WL [ $\text{mg cm}^{-2} \text{ h}^{-1}$ ]	E [%]
BS	0.051	-
$10^{-6}$	0.032	37.1
$10^{-5}$	0.031	39.2
$10^{-4}$	0.019	41.5
$10^{-3}$	0.017	43.5

It can be observed, that the presence of DMA reduce the copper dissolution in strongly acid solution, according to an inhibition efficiency higher than 40% obtained for  $10^{-3}$  M inhibitor, that suggests a good inhibition ability to form coordinative bonds and adsorption on the metal surface, respectively.

### 3.5. Surface analysis

The surface morphology of copper samples was analyzed after corrosive attack in the absence and presence of  $10^{-3}$  M DMA during 240 h immersion time. Figure 8 shows the SEM images recorded for copper samples at different magnifications.

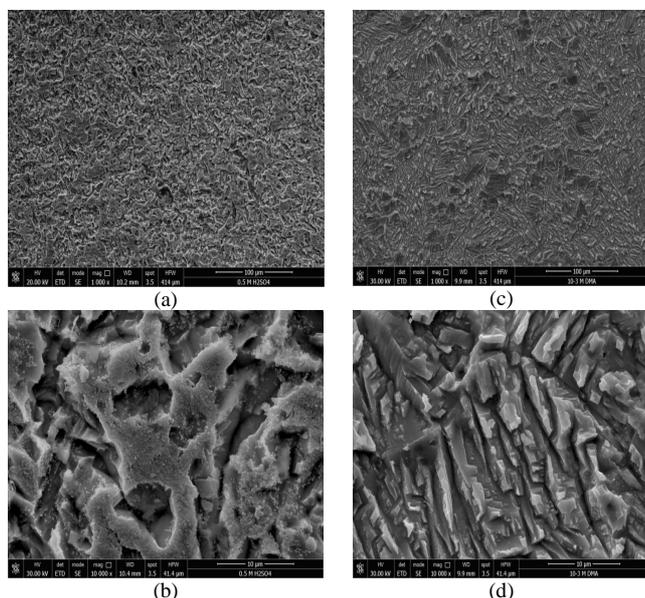


Figure 8. SEM images of copper samples after 240 h immersion time at different magnifications: (a,b) 0.5 M  $H_2SO_4$  and (c,d)  $10^{-3}$  M DMA

In the absence of DMA, damaged surface was observed due to its high dissolution rate of copper in 0.5 M  $H_2SO_4$  solution.

## 4. Conclusions

In this study the inhibition effect of different concentrations of DMA on copper corrosion process at different temperatures (308, 318, 328, 338 K) was investigated. The weight loss data were determined by gravimetric method in the absence and presence of different amounts of DMA, which allowed determination of inhibition efficiencies and surface coverage.

Despite the fact that previous experimental data [9] confirm the DMA catalytic effect for hydrogen evolution reaction, in the case of copper corrosion inhibition, DMA was efficient in sulphuric acid. The inhibiting action of this compound can be attributed to its interaction with the copper surface via its adsorption and blocking by organic molecules the anodic area where metallic copper ionization takes place. Also, the obtained Tafel diagrams confirm that DMA is an anodic type of corrosion inhibitor, acting on metal dissolution process, which are associated with cathodic hydrogen evolution reaction.

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