

THE POSSIBILITY OF COPPER CORROSION PROTECTION IN ACIDIC MEDIA USING A THIAZOLE DERIVATIVE

MOŽNOST PROTIKOROZIJSKE ZAŠČITE BAKRA V KISLEM MEDIJU Z UPORABO DERIVATOV TIAZOLA

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Assessing financial losses on an annual scale, it was determined that the world economy loses about 2.2 trillion US dollars as a result of the corrosion of materials. The most significant losses are caused by the corrosion of metals. Against corrosion, metals can be protected in several ways: by cathodic protection or anodic protection, by the use of inhibitors, or by using various protective coatings that can be metallic, non-metallic, organic or inorganic. In this paper, the possibility of the corrosion protection of copper was investigated in acidic media using inhibitors. The inhibitor properties of 5-(4'-dimethylamino-benzylidene)-2,4-dioxotetrahydro-1,3-thiazole, (DABDT) were tested on copper corrosion in an acidic sulphate-containing solution (0.1 mol dm⁻³ Na₂SO₄, pH = 3). Using potentiostatic polarization measurements, the inhibitor efficiency of DABDT as a function of concentration was determined and the mechanism of its adsorption on the copper surface was defined. It was found that the DABDT thiazole derivative acts as mixed inhibitor on copper corrosion in acidic media. In the investigation range, increasing the concentration results in a better inhibition efficiency of the DABDT.

Keywords: copper, corrosion, thiazole derivatives, polarization measurements

Ocena finančnih izgub na letnem nivoju je pokazala, da svetovna ekonomija izgubi okoli 2,2 milijardi ameriških dolarjev kot posledico korozije materialov. Najpomembnejše izgube so povzročene s korozijo kovin. Proti koroziji lahko kovine zaščitimo na več načinov: s katodno oziroma anodno zaščito, z uporabo inhibitorjev ali različnih zaščitnih prevlek, ki so lahko kovinske, nekovinske, organskega oziroma anorganskega izvora. V tem prispevku je bila raziskana možnost protikorozijske zaščite bakra v kislem mediju z uporabo inhibitorjev. Lastnosti inhibitorja iz 5-(4'-dimetilaminobenziliden)-2,4-dioksotetrahidro-1,3-tiazol, (DABDT), so bile preizkušene pri koroziji bakra v kislem mediju, ki je vseboval raztopino (0,1 mol dm⁻³ Na₂SO₄, pH = 3). S potencioštatičnimi meritvami polarizacije je bila določena učinkovitost DABDT kot funkcija koncentracije in mehanizem njegove adsorpcije na površino bakra. Odkrili smo, da se DABDT-derivati tiazola vedejo kot mešani inhibitorji pri koroziji bakra v kislem mediju. V raziskanem območju se je z naraščanjem koncentracije DABDT izboljšala učinkovitost zadrževanja korozije.

Ključne besede: baker, korozija, derivati tiazola, meritve polarizacije

1 INTRODUCTION

In accordance with recent estimates it has been calculated that the effect of corrosion on the US economy in 2012 exceeds 1 trillion dollars per year for the first time.¹ Taking into account this fact, it is clear that corrosion is the cause of significant losses in the economy of each country and therefore falls within one of the important factors of the global financial and energy crisis. It is understandable, therefore, that the great interest and tendency to reduce losses as a result of the corrosion of construction materials is to be kept to a minimum.

Copper and its alloys have good characteristics and a wide range of industrial applications. They have the largest number of applications as conductors of electricity and heat. Copper shows excellent performance as a structural material, because among other things, it is resistant to corrosion over a wide range of pH values. However, it is known that in aggressive media, copper is susceptible to corrosion, due to the lack of a protective

passive layer in the acidic environment². Copper as a structural material is often exposed to acidic conditions, e.g., during its purification, electro polishing or during the removal of corrosion products from the heat transmissions. The most commonly used acid in these processes is sulphuric acid. The protection of copper in these processes in an acidic environment is usually accomplished with corrosion inhibitors.³⁻⁵

Organic compounds that contain hetero-atoms such as nitrogen, sulphur and oxygen, or conjugated double bonds have shown good inhibition properties against copper corrosion.⁶⁻⁸ This kind of organic molecules can be adsorbed at the metal-solution interface, which will reduce the corrosive attack on the metal in acidic media.^{9,10}

The degree of corrosion protection of these molecules depends on the strength of the interaction between the organic molecule and the metal surface atoms.

The thiazole derivatives are an interesting group of nitrogen- and sulphur-containing organic compounds

that act as inhibitors against the dissolution of copper in acidic electrolytes.

The aim of this study is to investigate and interpret how the thiazole derivative 5-(4'-dimethylaminobenzylidene)-2,4-dioxotetrahydro-1,3-thiazole, (DABDT), inhibits the copper corrosion in aerated 0.1-M Na₂SO₄ at pH = 3.

2 EXPERIMENTAL

Reagent-grade chemicals (Merck) and double-distilled water were used to prepare the electrolyte of 0.1-M Na₂SO₄ at pH = 3; the pH was adjusted to 3.0 using diluted sulphuric acid.

The investigated thiazole derivative was 5-(4'-dimethylaminobenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (DABDT) (**Figure 1**).

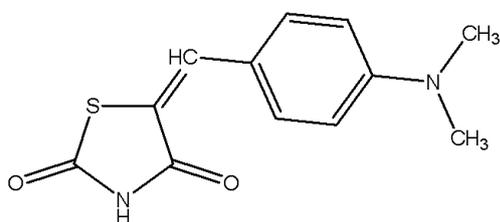


Figure 1: Structure of the investigated thiazoles

Slika 1: Struktura raziskanih tiazolov

All the experiments were conducted in the open atmosphere and at room temperature. Due to the low solubility of the tested thiazole derivative, the inhibitor was first dissolved in 20 ml of ethanol.

Weight-loss measurements were carried out on copper coupons (6 cm × 1.5 cm × 0.2 cm) in 0.1 mol dm⁻³ Na₂SO₄ at pH = 3 for different inhibitor concentrations (0.001 mmol dm⁻³–0.01 mmol dm⁻³). The coupons immersed in the test solutions were allowed to stand for one week in an air atmosphere.

For the electrochemical measurements a three-electrode cell was used. High-purity copper rods (99.99 % Cu) with an exposed area of 0.7 cm² were used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode and platinum was used as the counter electrode. Before using, the working electrode was wet-polished with SiC papers (grit sizes of 800 and 1200), rinsed with acetone and double-distilled water. All the measurements were made at room temperature.

The polarization measurements were performed at five different inhibitor concentrations in the concentration range 0.001–0.01 mmol dm⁻³. The measurements were carried out when the open-circuit potential (OCP) was stabilized at 5 mV/5 min. The potential was scanned between the OCP and 300 mV/SCE in both the cathodic and anodic directions at a scan rate of 10 mV min⁻¹. A PC-controlled potentiostat (VoltaLab PGZ 301) was applied.

3 RESULTS AND DISCUSSION

3.1 Weight-loss measurements

A weight-loss measurement for monitoring a metal's corrosion rate is a very usefully technique because of its simplicity and reliability.¹¹ The weight losses of the copper electrodes were determined after 7 d of immersion in the blank (0.1 mol dm⁻³ Na₂SO₄, pH = 3) and the inhibitor-containing solutions. Table 1 shows the weight loss of copper and the protection efficiency of the investigated thiazole derivative.

The protective efficiency, η/%, of the DABDT molecules was calculated using the following equation:¹²

$$\eta(\%) = \frac{W_0 - W}{W_0} \cdot 100$$

where W₀ and W are the weight losses of the copper coupons in the blank and inhibitor-contains solutions.

Table 1: Results of weight-loss measurements

Tabela 1: Rezultati meritev zamanjšanja mase

c /mmol dm ⁻³	W/mg cm ⁻²	η/%
0	1.54	–
0.001	0.80	48
0.003	0.54	65
0.005	0.25	84
0.007	0.20	87
0.01	0.14	91

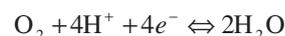
It is clear from **Table 1** that the corrosion rates were reduced in the presence of the DABDT derivate. The inhibition efficiency, as given in **Table 1**, is found to increase with the increase in the concentration of the inhibitors.

3.2 Potentiostatic measurements

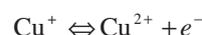
Potentiostatic polarization measurements were performed to determine the optimal concentration of DABDT and its inhibition efficiency on copper corrosion in acidic media (pH = 3). The polarization measurements were in the range of the concentration 0.001 mmol dm⁻³ to 0.01 mmol dm⁻³ at the room temperature.

Figure 2 shows the anodic and cathodic polarization plots of the copper electrode in the blank and inhibitor-containing solution (c = 0.05 mmol dm⁻³).

The obtained polarization curve in the blank and the inhibitor-containing solution are typical for copper in an acidic solution. The cathodic part of the polarization curves related to the oxygen reduction reaction:



and the anodic part related to the copper dissolution:



In the blank solution, at low over potentials, the cathodic polarization curves are linear but after approxi-

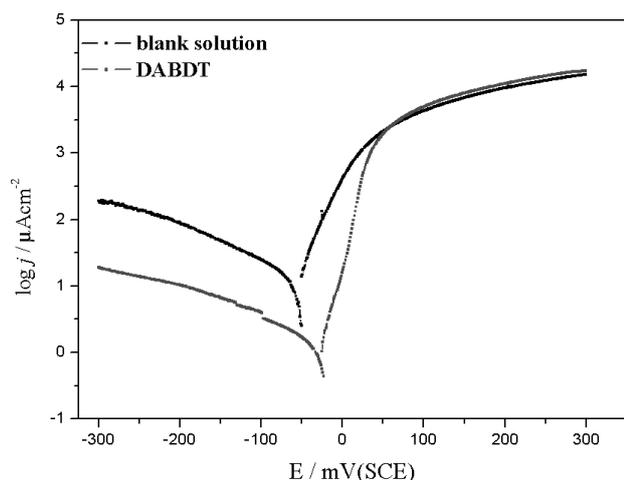


Figure 2: Polarization curves for copper electrodes with and without the thiazole derivatives ($c = 0.005 \text{ mmol dm}^{-3}$)

Slika 2: Polarizacijske krivulje za bakrove elektrode brez derivatov tiazola in z njimi ($c = 0.005 \text{ mmol dm}^{-3}$)

mately -300 mV/SCE the dependence begins to deviate from linear due to diffusion phenomena, and in these fields the measurements were not made. In the anodic part of the curve a significant dissolution of copper is evident. As **Figure 2** shows, the presence of the DABDT thiazole derivative induced a significant decrease in the cathodic current density and at low over-potentials there is an insignificantly small reduction of the anodic current density. It can be concluded that the investigated thiazole acts primarily as a cathodic inhibitor against copper corrosion, hindering the oxygen reduction reaction in acidic media. The inhibitor's presence in the corrosion solution does not cause a large shift of the corrosion potential.

In **Table 2** are the electrochemical parameters, such as the corrosion potential (E_{corr}) and the corrosion current density (j_{corr}), which were obtained by Tafel extrapolating the anodic and cathodic parts of the polarization curves and the inhibitor efficiency of the DABDT molecule.

The inhibitor efficiency of the DABDT molecule was calculated using the following equation:

$$\eta(\%) = \frac{j_0 - j}{j_0} \cdot 100$$

where, j_0 and j are the corrosion-current density measured on the copper electrode in the blank and inhibitor-containing solutions.

The obtained results are comparable with those calculated from the weight loss measurement (**Table 1**). A small difference can be observed with several authors.^{13–15} This difference can be attributed to the fact that a gravimetric measurement gives an average corrosion rate, whereas instantaneous corrosion rates were obtained using polarization methods.

As can be seen from **Table 2** the corrosion rate in the presence of DABDT molecules depended on the concentration of the thiazole. The inhibitor efficiency

Table 2: Electrochemical parameters of copper corrosion in the presence of different concentrations of DABDT

Tabela 2: Elektrokemijski parametri korozije bakra v različnih koncentracijah DABDT

$c/\text{mmol dm}^{-3}$	$E_{\text{corr}}/\text{mV}$	$j_{\text{corr}}/\mu\text{A cm}^{-2}$	$\eta/\%$
0	-58	14.16	–
0.001	-18	7.71	46
0.003	-11	4.87	66
0.005	-20	2.74	81
0.007	-12	1.61	89
0.01	-26	1.54	90

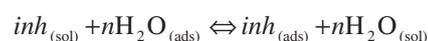
Table 3: Copper surface coverage in a different inhibitor concentration

Tabela 3: Obseg prekritja površine bakra pri različnih koncentracijah inhibitorja

$c/\text{mmol dm}^{-3}$	θ
0.001	0.455
0.003	0.656
0.005	0.807
0.007	0.886
0.01	0.898

increased with the increase in the concentration of thiazole. In the investigated concentration range, the maximum concentration of $0.01 \text{ mmol dm}^{-3}$ produced the best inhibitor efficiency. A higher concentration of inhibitor could not be tested because of the low solubility of the DABDT. The increasing inhibitor efficiency with the concentration indicates that DABDT molecules protecting the copper from corrosion via the adsorption onto the metal surface.

During the adsorption onto the metal surface the inhibitor molecules are replacing the water molecules that are pre-adsorbed at the metal surface. According to Bockris,¹⁶ the adsorption of an organic molecule at the metal/solution interface may be written according to the following displacement reaction:



where n is the number of water molecules removed from the metal surface for each molecule of adsorbed inhibitor. The interactions of the organic molecules at the electrical double layer change its properties and structure. Changes in the structure of the electric double layer occur due to the fact that the inhibitor molecules are larger than the water molecules. Organic molecules also have a lower value of the dielectric constant than the water molecules, which reflects in the properties of the double layer as the reduction of its conductivity. Adsorption isotherms provide information about the interaction among the adsorbed molecules themselves and their interactions with the electrode surface.¹⁷ The values of the degree of surface coverage, θ , (**Table 3**) calculated from the following equation¹⁸:

$$\theta = 1 - \frac{j}{j_0}$$

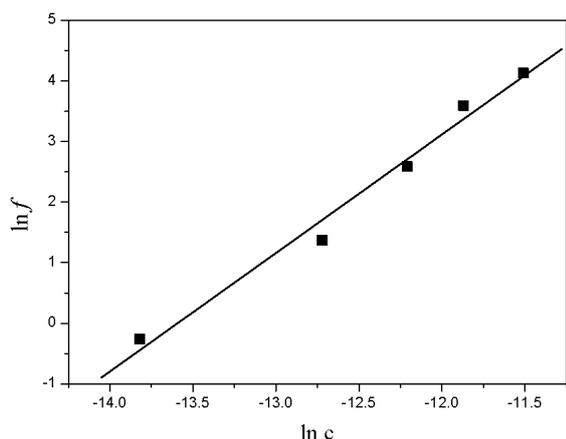


Figure 3: Bockris-Swinkels isotherms
Slika 3: Bockris-Swinkelsove izoterme

were used to determine the isotherm that best describes the adsorption process.

The best correlation between the experimental results and the isotherms described above was obtained using Bockris-Swinkels isotherm:^{16,4}

$$\frac{\left[\frac{\theta}{(1-\theta)^n} \right]^{\theta+n(1-\theta)^{n-1}}}{n^n} = Kc$$

where θ is the surface coverage, n is the number of water molecules substituted, c is the inhibitor concentration and K is the constant of the adsorption process.

Figure 3 shows the Bockris-Swinkels isotherms obtained from copper in the presence of different concentrations of thiazole, where f is equal to the left part of the Bockris-Swinkels isotherms,

Knowing the value of K provides the possibility of calculating the basic thermodynamic parameter, the standard free energy of the adsorption is ΔG_{ads} . The constant of adsorption, K , is related to the standard free energy of adsorption, ΔG_{ads} , with the following equation:¹⁹

Table 4 reports the data from Bockris-Swinkels isotherm and the value of ΔG_{ads} for the adsorption process of the investigated thiazole derivative.

Table 4: Value of the adsorption constant, K , the number of replacement water molecules, n , the regression coefficient, R , and the standard free energy of adsorption, ΔG_{ads} , for the DABDT molecule

Table 4: Vrednosti adsorpcijske konstante K , število nadomeščenih molekul vode n , regresijski koeficient R in standardna prosta energija adsorpcije ΔG_{ads} za molekulo DABDT

$\ln K$	n	$\Delta G_{ads}/\text{kJ mol}^{-1}$	R
13.55	1	-43.5	0.981

The high value of the adsorption constant, K , indicates that the adsorption process of the DABDT molecules takes place relatively quickly on the copper surface. The results in **Table 4** show that the DABDT molecule is adsorbed on the copper surface, replacing one molecule of water. The number of water molecules

that is replaced can be seen as an indicator of the position of the inhibitor molecules on the surface of the copper. The small number of water molecules suggests that the thiazole molecules are vertically oriented in relation to the copper surface.

The negative values of ΔG_{ads} ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the copper surface. Generally, the values of ΔG_{ads} are used to determine the type of interaction between the organic molecules and the metal surface atoms. It is well known that the values of ΔG_{ads} of the order of -20 kJ mol^{-1} or lower indicate physisorption; those of order of -40 kJ mol^{-1} or higher involve charge sharing or a coordinate type of bond between metals and organic molecules.^{20,21} In case of DABDT molecules the calculated values of ΔG_{ads} are slightly more negative than -40 kJ mol^{-1} , and therefore indicate that the adsorption mechanism of this thiazole derivative on copper in acidic sulphur-containing media was typically chemisorption.

The ability to form a chemical bond with copper and the good inhibition efficiency of the DABDT molecules (90 %) can be explained by the characteristics of dimethyl-amino groups, which are present in the molecule at position 5. In the DABDT molecule the dimethyl-amino group has a great influence on the distribution of the electron density around the active site of the thiazole molecule and therefore its inhibitor activity. The dimethyl-amino group has a positive inductive and resonance effect. These effects are powerful electron-donating effects, providing an increase of the electron density of the active centre of the thiazole molecules (sulphur atom). According to this the unshared pair of electrons in the sulphur atom can strongly interact with the copper uncompleted d-orbitals to provide a protective chemisorption film and better copper protection in the acidic media.

4 CONCLUSION

In this paper the possibility of the corrosion protection of copper in acidic media using a DABDT derivative was investigated in an acidic sulphate-containing solution ($0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, $\text{pH} = 3$) using potentiostatic polarization measurements.

From the obtained results, it can be concluded:

1. The investigated derivative, DABDT, shows a good inhibition efficiency (90 %) towards the copper corrosion in the acidic sulphate-containing solution.
2. DABDT acts as a mixed copper corrosion inhibitor. Compared to the blank solution in the presence of these molecules there is a slowdown in the cathodic reaction as well as the anodic process of the metal dissolution.
3. The best inhibition efficiency was obtained for the concentration $0.01 \text{ mmol dm}^{-3}$.

4. DABDT protects the copper surface from corrosion by adsorption.
5. The adsorption of these molecules on the copper surface happens as a fast and spontaneous process, following the Bockris-Swinkels isotherms by replacing one water molecule on the copper surface.
6. Adsorption leads to the formation of a chemical bond between the thiazole derivative DABDT and the copper atoms.
7. There is a good inhibition efficiency of the tested compound achieved due to the presence of strong electron-donating $N(CH_3)_2$ groups.

Acknowledgments

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