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5-chloro-1H-benzotriazole and potassium sorbate as binary corrosion inhibitor of copper in acidic solution

ABSTRACT

The effect of potassium sorbate as well as 5-chloro-1H-benzotriazole – potassium sorbate on the corrosion behavior of copper in acidic sulfate media containing Cl⁻ ions was examined. For this purpose, the electrochemical methods and quantum chemical calculations were used. The inhibition efficiency in the presence of 5-chloro-1H-benzotriazole – potassium sorbate was higher than in the presence of potassium sorbate. Also, the inhibition efficiency of binary inhibitor depends on the concentration of Cl⁻ ions added in sulfate solution. According to the results obtained by potentiodynamic polarization measurements, both potassium sorbate and 5-chloro-1H-benzotriazole – potassium sorbate behave as mixed type inhibitors. Quantum chemical parameters are in good agreement with results obtained by electrochemical measurements.
Keywords: *inhibition efficiency, 5-chloro-1H-benzotriazole, potassium sorbate, quantum chemical calculations, electrochemical measurements.*

1. INTRODUCTION

Due to its good properties, copper is used as electric and heat conductor in different industries and also its wires are used in cables in household. Copper is resistant to certain chemicals, but aggressive solutions containing SO_4^{2-}, NO_3^-, Cl^- ions, cause its dissolution. Even trace amounts of Cl^- ions can cause the dissolution process of copper [1]. Having that in mind, researchers are focused on finding a suitable corrosion inhibitor in order to protect metals surfaces. In accordance with previous researches, the best protection of metal is achieved by using organic compounds as inhibitors. Different organic compounds including azoles [2-7], amino acids [8-14], plant extracts [15-18] and organic dyes [19, 20] are examined as potential corrosion inhibitors in various environ-ments. It is observed that their inhibitory activity is based on the formation of coordinating bond bet-ween vacant d orbital of metal and a lone electron pair of the corresponding heterocyclic compounds [21, 22].

In addition to the molecular structure of compound, other experimental parameters such as temperature, pH value and immersion time have influence on the reduction of corrosion rate [23-25]. Abelev et al. [26] and Nagar et al. [27], in their researches, have determined the inhibitory ability of potassium sorbate against copper corrosion. The corrosion rate of copper in neutral and alkaline solutions is reduced due to the formation of hydrophobic protective film on the metal surface.

According to the relevant literature [28], chloride ions increase the rate of copper dissolution. Having that in mind, it is interesting to examine the corrosion behavior of copper in acidic solution containing both SO_4^{2-} and Cl^- ions. Also, this paper deals with investigation of potassium sorbate (PS) and binary system containing 5-chloro-1H-benzotriazole and potassium sorbate (CBTAH – PS) as corrosion inhibitors of copper in acidic medium with simultaneous presence of chloride and sulfate ions.

2. MATERIALS AND METHODS

2.1. Electrochemical measurements

The working electrode of copper with exposed surface area of 0.49 cm², was prepared as follows: the copper wire was cut and sealed using a cold sealing material based on methyl methacrylate. Before the beginning of each measurement

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process, copper electrode was polished with alumina (0.3μm Al₂O₃, Buehler USA), washed with distilled water and dried.

For electrochemical testing of the corrosion behavior of copper potentiostat (IVIUM XRE, IVIUM Technologies) with the appropriate software was used. The system is made up of three electrodes, copper electrode as working, platinum as the auxiliary electrode and standard calomel electrode as the reference electrode.

The electrochemical methods used for this research were: open circuit potential (OCP) measurements, potentiodynamic polarization measurements and cyclic voltammetry. Potentiodynamic polarization was recorded from the open circuit potential to - 0.25 V (vs SCE) in cathodic and to 0.20 V (vs SCE) in anodic direction, while the cyclic voltammetry was recorded in a wider potential range from -1 V (vs SCE) to 1 V (vs SCE). Scan rate was 1 mV/s for potentiodynamic measurements and 10mV/s for cyclic voltammetry measurements.

For the preparation of tested solutions the following compounds were used: sulfuric acid (H₂SO₄, Zorka Pharmacy, Sabac, Serbia), hydrochloric acid (HCl, Zorka Pharmacy, Sabac, Serbia), 5-chloro-1H-benzotriazole (Sigma-Aldrich, Germany) and potassium sorbate (Sigma-Aldrich, Germany). Hydrochloric acid (37 mass %) was added to 0.01 M H₂SO₄ solution in order to obtain 0.05 M Cl⁻ solution.

2.2. Analysis of copper samples surface by scanning electron microscopy

The copper surface was examined after exposing the sample to an acidic sulfate solution (0.01 M H₂SO₄), in the presence of potassium sorbate + $5 \cdot 10^{-2}$ M Cl⁻ as well as in the presence of CBTAH + potassium sorbate + $5 \cdot 10^{-2}$ M Cl⁻ for a period of 7 days. The tests were conducted by using a scanning electron microscope Tescan VEGA 3 LM with Oxford EDS X-act 350 Inca system.

3. RESULTS AND DISCUSSION

3.1. The open circuit potential measurements of copper

Primarily, copper electrode was subjected to determination of the open circuit potential values (OCP) in the blank solution and in inhibited solutions with the addition of different concentrations of Cl⁻ ions. The obtained results are shown in Fig 1. The presence of different concentration of Cl⁻ ions in sulfate solution has influence on OCP values. Actually, the addition of Cl⁻ ions leads to displacement of OCP toward negative direction in regard to inhibitor free solution

(E_{OCP} = -0.03 V vs. SCE). This could be explained by the adsorption of Cl⁻ ions on the copper surface and formation of CuCl species which leads to more negative charge [29, 30]. Similar results are obtained in the presence of investigated inhibitors, PS and CBTAH – PS. However, the change of the OCP values in the presence of inhibitors is not higher than 85 mV (vs. SCE). Thereby, these compounds have influence on both anodic and cathodic reactions [31] which will be discussed later.
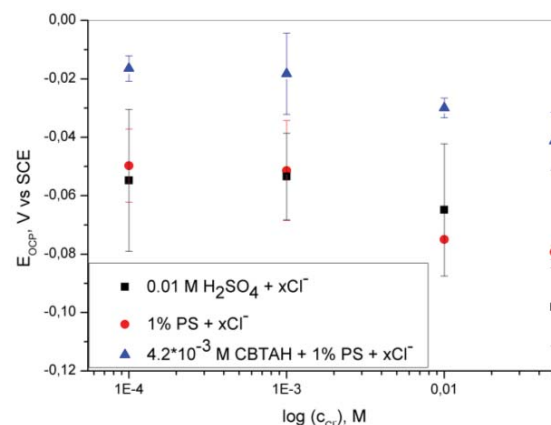

Figure 1. Open circuit potential of copper in 0.01 M H₂SO₄ in the presence of different concentrations of Cl⁻ ions and in the presence of 1% potassium sorbate as well as $4.2 \cdot 10^{-3}$ M CBTAH with 1% potassium sorbate

Slika 1. Potencijal otvorenog kola bakra u 0,01 M H₂SO₄ u prisustvu različitih koncentracija Cl⁻ jona, i sa dodatkom 1% kalijum-sorbata kao i $4,2 \cdot 10^{-3}$ M CBTAH + 1% kalijum-sorbat

3.2. Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were carried out after the determination of OCP values. Experiments were conducted in acidic sulfate solution in the presence of Cl⁻ ions as well as in inhibited solutions with the addition of Cl⁻ ions. Electrochemical parameters of copper corrosion such as corrosion potential (E_{corr}), corrosion current density (j_{corr}), anodic (b_a) and cathodic (b_c) Tafel slopes and inhibition efficiency (IE) are calculated based on the polarization curves and summarized in Table 1.

The inhibition efficiency is calculated according to the equation (1):

$$\%IE = 100 \cdot [(j_{corr} - j_{corr(inh)}) / j_{corr}] \quad (1)$$

Where j_{corr} and $j_{corr(inh)}$ are the corrosion current densities in the absence and presence of investigated inhibitors.

The addition of different concentrations of Cl⁻ ions in 0.01 M H_2SO_4 solution (Fig 2 and Table 1) leads to displacement of E_{corr} into negative direction, which was also observed in earlier investigation by Kear et al. [32]. By analyzing the corrosion current density, it is noted that this value increases with the concentration of Cl⁻ ions thereby the corrosion rate of copper increases, too. In accordance with the obtained results, Cl⁻ ions act as activators of copper dissolution. Similar results were obtained by El-Sherif et al. [33].
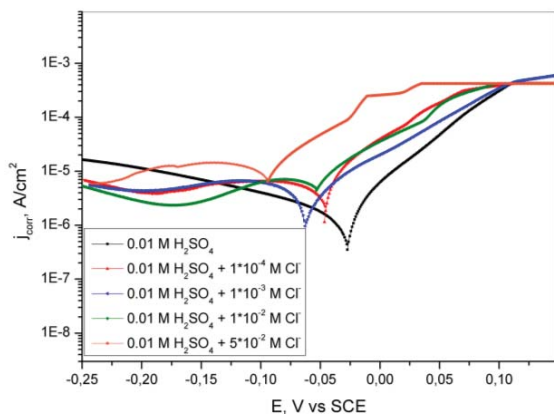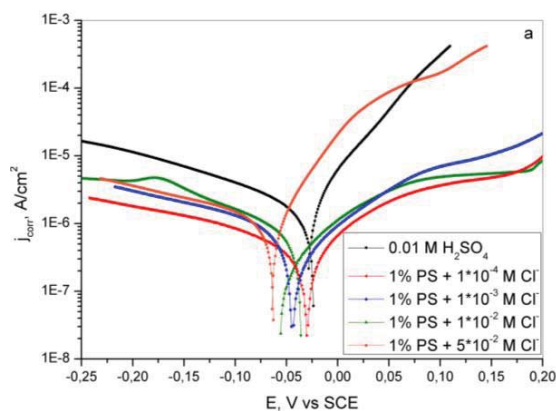

Figure 2. Potentiodynamic polarization curves of copper in 0.01 M H_2SO_4 and with the addition of different concentrations of Cl⁻ ions
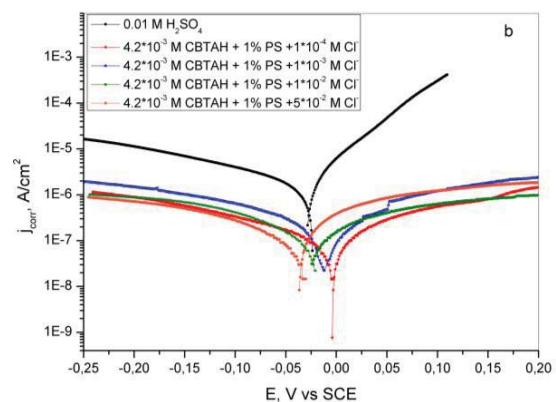
Slika 2. Potenciodinamičke polarizacione krive bakra u 0,01 M H_2SO_4 i u prisustvu različitih koncentracija Cl⁻ jona

The influence of PS on the corrosion behavior of copper in acidic solution containing both SO_4^{2-} and Cl⁻ ions is investigated. According to the Fig 3a, in the presence of PS, E_{corr} did not significantly shift toward negative values. Also, the addition of PS causes the displacement of both anodic and cathodic curves toward lower current density except for the concentration of $5·10^{-2}$ M Cl⁻. In this case, PS has more pronounced effect on the cathodic reaction. By analyzing the corrosion current density in Table 1, it can be seen that this value decreased with the addition of PS. However, the concentration of Cl⁻ ions has influence on the inhibition effect of PS; as concentration of Cl⁻ ions increases, the inhibition effect of PS decreases. It is proposed that Cl⁻ ion, which has small diameter, can penetrate through the formed layer and cause the further dissolution of metal. In order to improve the inhibition efficiency, binary inhibitor system containing CBTAH – PS was investigated. As can be seen from the Fig 3b, in the presence of CBTAH – PS the corrosion current density was lower in

comparison to blank solution and also in comparison to inhibited solution with only PS. This indicates the formation of protective layer of CBTAH - PS on the metal surface. In the presence of binary inhibitor, the E_{corr} has not moved significantly into negative direction. Also, both anodic and cathodic current densities are reduced due to the adsorption of inhibitor molecules on the copper surface. It can be said that CBTAH - PS behaves like mixed type inhibitor [5, 34]. According to the results presented in Table 1, both anodic and cathodic Tafel slopes are changed in the presence of binary inhibitor indicating that the formed layer has a good protective effect [35]. It is proposed that Cl⁻ ions are included in the formation of protective layer.

a)

b)

Figure 3. Potentiodynamic polarization curves of copper in 0.01 M H_2SO_4 and with the addition of different concentrations of Cl⁻ ions in the presence of (a) 1% potassium sorbate (b) $4.2·10^{-3}$ M CBTAH + 1% potassium sorbate

Slika 3. Potenciodinamičke polarizacione krive bakra u 0,01 M H_2SO_4 u prisustvu različitih koncentracija Cl⁻ jona, i sa dodatkom (a) 1% kalijum-sorbata; (b) $4,2·10^{-3}$ M CBTAH + 1% kalijum-sorbat

Table 1. Electrochemical parameters of copper corrosion in 0.01 M H₂SO₄ without and with the addition of different concentration of Cl⁻ ions

Tabela 1. Elektrohemijski parametri korozije bakra u 0,01 M H₂SO₄ bez i sa dodatkom različitih koncentracija Cl⁻ jona

Medium		E_{corr}, V (vs. SCE)	j_{corr}, µA/cm²	b_a, V/dec	$-b_c$, V/dec	IE, %
0.01 M H₂SO₄	/	-0.030	1.84	0.045	0.136	/
0.01 M H₂SO₄	1·10⁻⁴ M Cl⁻	-0.043	4.24	0.081	0.132	/
0.01 M H₂SO₄	1·10⁻³ M Cl⁻	-0.048	4.90	0.086	0.152	/
0.01 M H₂SO₄	1·10⁻² M Cl⁻	-0.059	5.35	0.086	0.117	/
0.01 M H₂SO₄	5·10⁻² M Cl⁻	-0.094	8.99	0.087	0.126	/

Table 2. Electrochemical parameters of copper corrosion in 0.01 M H₂SO₄ without and with the addition of inhibitors, in the presence of different concentration of Cl⁻ ions

Tabela 2. Elektrohemijski parametri korozije bakra u 0,01 M H₂SO₄ bez i sa dodatkom inhibitora, u prisustvu različitih koncentracija Cl⁻ jona

| Medium			E_{corr}, V (vs. SCE)	j_{corr}, µA/cm²	b_a, V/dec	$-b_c$, V/dec	IE, %
0.01 M H₂SO₄			-0.030	1.84	0.045	0.136	/
/	1% potassium sorbate	1·10⁻⁴ M Cl⁻	-0.031	0.400	0.095	0.075	78.2
		1·10⁻³ M Cl⁻	-0.043	0.469	0.119	0.252	74.5
		1·10⁻² M Cl⁻	-0.045	0.653	0.161	0.167	64.5
		5·10⁻² M Cl⁻	-0.064	0.784	0.043	0.117	57.4
4.2·10⁻³ M CBTAH	1% potassium sorbate	1·10⁻⁴ M Cl⁻	-0.0029	0.0426	0.054	0.072	97.7
		1·10⁻³ M Cl⁻	-0.012	0.0447	0.045	0.037	97.5
		1·10⁻² M Cl⁻	-0.023	0.0613	0.065	0.070	96.7
		5·10⁻² M Cl⁻	-0.035	0.0685	0.088	0.097	96.3

3.3. Cyclic voltammetry measurements

The electrochemical behavior of Cu in blank solution without and with the addition of inhibitors in the presence of Cl⁻ ions is examined by cyclic voltammetry (Fig 4 and 5). According to the curve obtained in blank solution, copper undergoes dissolution to Cu⁺ ions [36]. In the reverse scan, cathodic peak is observed which indicates a reduction of generated copper ions [37].

In naturally aerated acidic sulfate solutions, the dissolution of copper takes place according to reactions (2) and (3) [38], while the reduction of dissolved oxygen occurs at the cathode (reaction 4) [39]:

$$Cu \rightarrow Cu^+ + e^- \qquad (2)$$

$$Cu^+ \rightarrow Cu^{2+} + e^- \qquad (3)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (4)$$
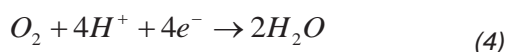
The presence of Cl⁻ ions in an acidic solution leads to copper corrosion by reaction (5) and formation of CuCl layer [32]:

$$Cu + Cl^- \rightarrow CuCl + e^- \qquad (5)$$
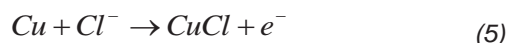
The formed CuCl layer does not provide copper protection due to its instability. Further, it reacts with Cl⁻ ions according to the reaction (6) and forms soluble complex CuCl₂⁻ [39]. In accordance with this, an increase of corrosion current density can be seen in CV curves (Fig 4) which indicates the acceleration of copper dissolution. Similar results are observed by potentiodynamic polarization measurements.

$$CuCl + Cl^- \rightarrow CuCl_2^- \qquad (6)$$
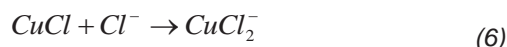
The effect of potassium sorbate on corrosion behavior of copper in acidic solution containing both sulfate and chloride ions, is shown in Fig 5a. The addition of potassium sorbate leads to inhibition of copper corrosion, but this effect decreases

with increasing concentration of chloride ions in solution. According to the literature [40], it is known that chloride ions have ability to penetrate through the formed layer which leads to further corrosion of metal. As can be seen, in the presence of $5 \cdot 10^{-2}$ M Cl⁻, the anodic current density gradually increases with increasing the potential value. It is assumed that the concentration of potassium sorbate is insufficient to protect copper against chloride attack.
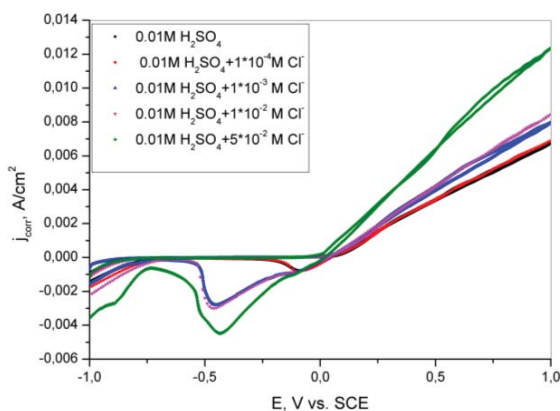

Figure 4. Cyclic voltammetric curves of copper in 0.01 M H₂SO₄ solution without and with the addition of different concentrations of Cl⁻ ions

Slika 4. Ciklični voltagram bakra u 0,01 M H₂SO₄ bez i sa dodatkom različitih koncentracija Cl⁻ jona

Similar results are obtained by potentiodynamic polarization measurements. In order to improve the degree of copper protection, experiments were carried out in acidic solution with the addition of both CBTAH and potassium sorbate. In the presence of binary inhibitor (Fig 5b), the corrosion current density has been significantly reduced in comparison to the inhibitor-free solution, which can be attributed to the adsorption of inhibitor on the active sites on the copper surface. Also, the cathodic peak is evident, which intensity decreased in the presence of CBTAH – potassium sorbate in comparison with acidic sulfate solution containing Cl⁻ ions. This indicates the inhibitory effect of the binary composition in the presence of different amounts of Cl⁻ ions. The observed cathodic peak probably indicates the reduction of CuCl₂⁻ [41]. Having in mind the ability of Cl⁻ ions to penetrate through the formed film and by analyzing the CV curves, it can be noticed that in the presence of the highest Cl⁻ concentration, current density gradually increases with the potential due to the adsorption of Cl⁻ ions. However, value of current density under this conditions is smaller than in blank solution. It is assumed that binary inhibitors provide good

protection of copper. Also, in the presence of binary inhibitor, anodic dissolution of copper occures at higher potential values (~ 0.5 V vs. SCE) in comparison to blank solution. This behavior suggests the formation of compact layer on the copper surface in the presence of CBTAH – PS. Similar observation was found by Szocs et al. [42].
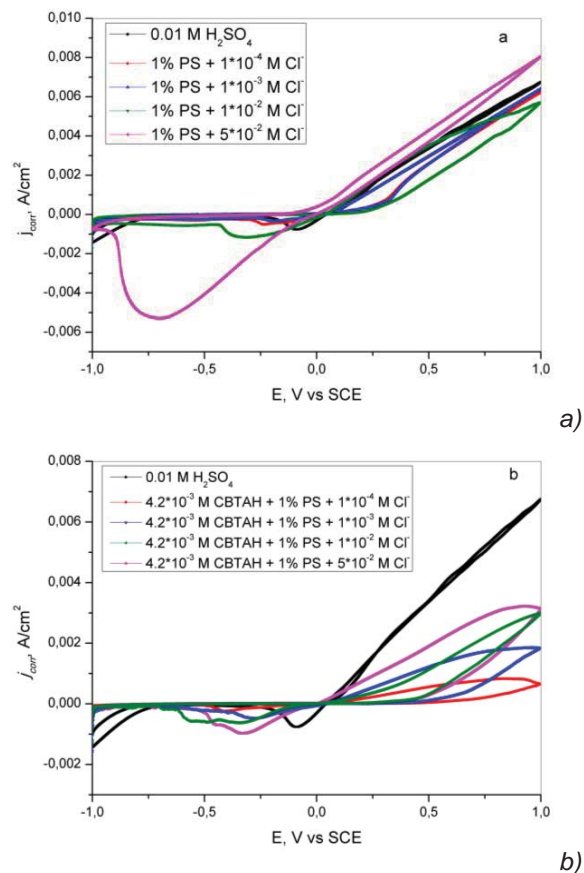

a)

b)

Figure 5. Cyclic voltammetric curves of copper in 0.01M H₂SO₄ in the presence of (a) 1% potassium sorbate and (b) 4.2·10⁻³ M CBTAH and 1% potassium sorbate with different concentrations of Cl⁻ ions

Slika 5. Ciklični voltagram bakra u 0,01 M H₂SO₄ u prisustvu različitih koncentracija Cl⁻ jona, i sa dodatkom (a) 1% kalijum-sorbata i (b) 4,2·10⁻³ M CBTAH + 1% kalijum-sorbat

3.4. The surface analysis (SEM-EDS) of copper specimens

The characterization of copper specimens after immersion in inhibitor free solution, PS - Cl⁻ ions and CBTAH – PS - Cl⁻ ions was carried out by scanning electron microscopy with energy dispersive spectroscopy (SEM – EDS). As can be seen in Fig 6, the surface has cracks due to the aggressive effect of sulfate ions on copper dissolution.
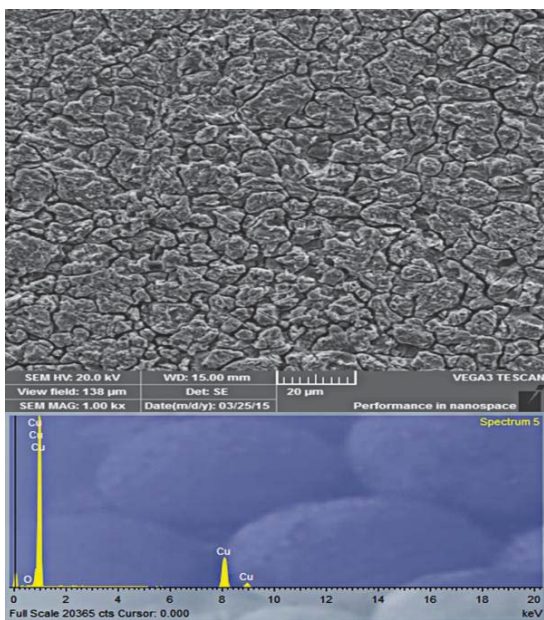
Figure 6. SEM micrograph and EDS spectrum of copper surface after treatment in 0.01 M H_2SO_4 for 7 days

Slika 6. SEM mikrografija i EDS spektar bakarne površine nakon tretiranja 7 dana u rastvoru 0,01 M H_2SO_4
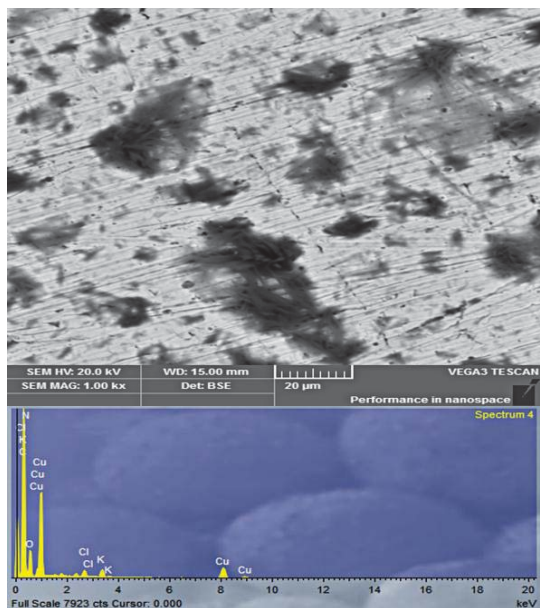

Figure 7. SEM micrograph and EDS spectrum of copper surface after treatment in 0.01 M H_2SO_4 in the presence of $4.2 \cdot 10^{-3}$ M CBTAH + 1% potassium sorbate + $5 \cdot 10^{-2}$ M Cl⁻ for 7 days

Slika 7. SEM mikrografija i EDS spektar bakarne površine nakon tretiranja 7 dana u rastvoru 0,01 M H_2SO_4 u prisustvu $4,2 \cdot 10^{-3}$ M CBTAH + 1% kalijum-sorbat + $5 \cdot 10^{-2}$ M Cl⁻

The corresponding EDS diagram contains peaks of Cu and O atoms, which indicates that copper dissolution takes place through the formation of oxides. In the presence of binary inhibitor, the copper surface is smoother due to the formation of protective layer which covers the copper surface (Fig 7). According to the EDS diagram (Fig 7), the appearance of peaks of atoms C and N indicates that the protective film is formed on the copper surface. Also, the intensity of these peaks is higher in comparison to the peaks recorded in the presence of only PS (Fig 8), which is in good agreement with the results obtained by electrochemical measurements.
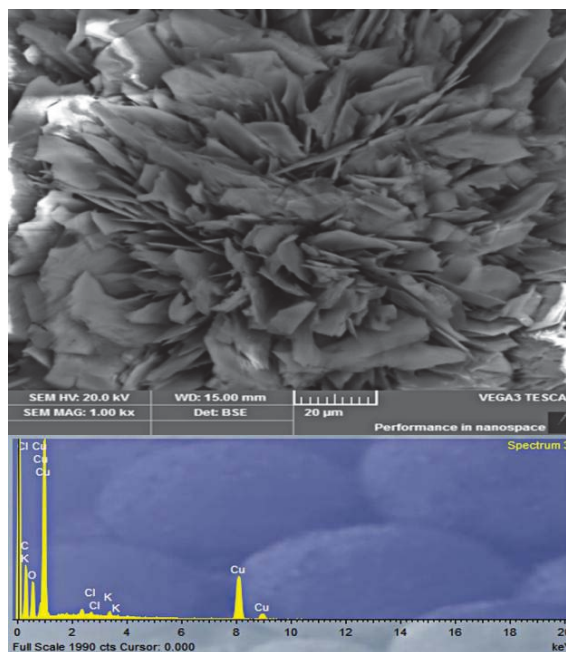

Figure 8. SEM micrograph and EDS spectrum of copper surface after treatment in 0.01 M H_2SO_4 in the presence of 1% potassium sorbate + $5 \cdot 10^{-2}$ M Cl⁻ for 7 days

Slika 8. SEM mikrografija i EDS spektar bakarne površine nakon tretiranja 7 dana u rastvoru 0,01 M H_2SO_4 u prisustvu 1% kalijum-sorbat + $5 \cdot 10^{-2}$ M Cl⁻

3.5. Quantum chemical calculations

In order to investigate the influence of molecular structure of inhibitors on corrosion process, quantum chemical calculations were performed using PM3-SCF method. The calculations and visualization are performed using the software ArgusLab 4.0 [43]. The high value of highest occupied molecular energy (E_{HOMO}) indicates an ability of the molecule to donate electrons while the low value of E_{LUMO} suggests the ability of molecule to accept electrons from appropriate donor

molecule. According to the relevant literature [44], a low value of dipole moment favors the accumulation of organic molecules on the copper surface thus the corrosion process is reduced. The HOMO and LUMO of both investigated compounds are illustrated in Fig 9-12. The calculated parameters including E_{HOMO}, E_{LUMO}, energy gap (ΔE), ionization potential (I), electron affinity (A), hardness (η), electronegativity (χ), dipole moment (μ) and fraction of electrons transferred (ΔN) are calculated according to equations (7) – (11) and shown in Table 3. According to presented parameters, it is clear that lower value of hardness and lower value of energy gap are obtained for CBTAH in comparison to the PS. These results are predicting the stronger adsorption of CBTAH on the copper surface which is in agreement with results obtained by electrochemical methods.

$$I = -E_{HOMO} \tag{7}$$

$$A = -E_{LUMO} \tag{8}$$

$$\chi = (I + A)/2 \tag{9}$$

$$\eta = (I - A)/2 \tag{10}$$

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})} \tag{11}$$

Where χ_{Cu} and η_{Cu} are the electronegativity and hardness of copper. The values of these parameters are 4.48 eV/mol and 0 eV/mol, respectively [45, 46].
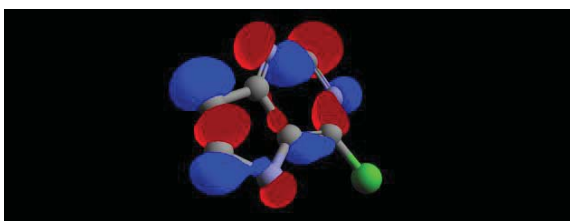

Figure 9. Distribution of HOMO of CBTAH
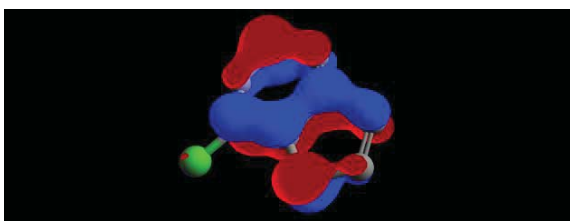
Slika 9. HOMO molekulske orbitale inhibitora CBTAH

Figure 10. Distribution of LUMO of CBTAH

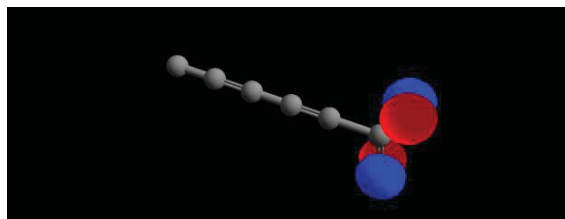*Slika 10. LUMO molekulske orbitale inhibitora CBTAH*

Figure 11. Distribution of HOMO of PS

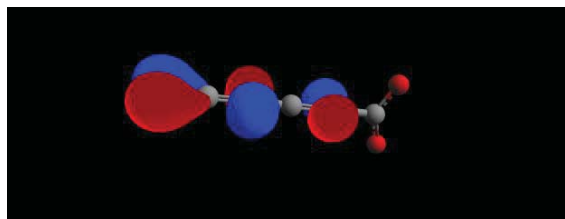*Slika 11. HOMO molekulske orbitale inhibitora PS*

Figure 12. Distribution of LUMO of PS

Slika 12. LUMO molekulske orbitale inhibitora PS

Table 3. Quantum chemical parameters

Tabela 3. Kvantno-hemijski parametri

Parameters	CBTAH	PS
E_{HOMO}, eV	-9.9580	-9.8736
E_{LUMO}, eV	-3.6716	-2.6787
ΔE, eV	6.2864	7.1949
I, eV	9.9580	9.8736
A, eV	3.6716	2.6787
χ, eV	6.8148	6.2761
η, eV	3.1432	3.5974
ΔN	-0.371	-0.250
μ, D	3.7439	10.7848

According to the Table 3, E_{HOMO} values indicate that CBTAH will adsorb more strongly on copper surface than PS, which is in agreement with relevant literature [47]. Also, the presence of -Cl substituent in position 5 of benzene ring affects the acidity on the hydrogen atom in position 2 due to electron withdraw characteristics of chlorine substituent. Further, the acidity of CBTAH molecule is increased and after the release of the hydrogen atom, the nitrogen atom at a position 2 presents the interaction site with copper surface. As a result, Cu-BTA layer is formed [48]. Thus, in the examined conditions, initially CBTAH is adsorbed on the copper surface followed by adsorption of PS molecules. Similar results are observed in literature dealing with relevant topic [49, 50].

4. CONCLUSION

In accordance with the conducted research it can be concluded:

- The addition of Cl^- ions in 0.01 M H_2SO_4 solution leads to acceleration of the corrosion of copper.

- Potassium sorbate behaves as inhibitor against copper dissolution in acidic solution containing both SO_4^{2-} and Cl^- ions. The achieved inhibition efficiency of potassium sorbate depends on concentration of Cl^- ions.

- The higher inhibition efficiency in the presence of binary inhibitor CBTAH – PS, in examined conditions, is achieved.

- SEM-EDS analysis confirmed the formation of protective layer on the copper surface in the presence of inhibitor.

- Quantum chemical calculations are in a good agreement with the results obtained by electrochemical measurements.

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IZVOD

5-HLOR-1H-BENZOTRIAZOL I KALIJUM-SORBAT KAO DVOKOMPONENTNI INHIBITOR KOROZIJE BAKRA U KISELOJ SREDINI

Ispitivan je uticaj kalijum-sorbata i dvokomponentnog inhibitora, 5-hlor-1H-benzotriazol – kalijum-sorbat, na koroziono ponašanje bakra u kiselom rastvoru sulfata u prisustvu Cl⁻ jona. Za navedeno istraživanje korišćene su elektrohemijske metode i kvantno-hemijski proračuni. Postignuta je veća vrednost efikasnosti inhibicije u prisustvu 5-hlor-1H-benzotriazol – kalijum-sorbat u odnosu na prisustvo samog kalijum-sorbata. Isto tako, efikasnost inhibicije dvokomponentnog inhibitora zavisi od koncentracije dodatih Cl⁻ jona kiselom rastvoru sulfata. U skladu sa postignutim rezultatima na osnovu potenciodinamičkih polarizacionih merenja, kalijum-sorbat i 5-hlor-1H-benzotriazol – kalijum-sorbat se ponašaju kao mešoviti tip inhibitora. Parametri dobijeni na osnovu kvantno-hemijskih proračuna su u saglasnosti sa rezultatima koji su postignuti elektrohemijskim merenjima.

Ključne reči: *efikasnost inhibicije, 5-hlor-1H-benzotriazol, kalijum-sorbat, kvantno-hemijski proračuni, elektrohemijska merenja*