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The Influence of pH and Chlorides on Electrochemical Behavior of Copper in the Presence of Benzotriazole

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The influence of benzotriazole on electrochemical behavior of copper in borax buffer solutions, in pH range 8.0-12.3, with or without 0.05 M NaCl chlorides, was studied. Two methods were used in order to examine the effect of BTA: a) the Cu electrode was immersed for various time periods (5, 15 and 60 min) in 0.2 % BTA solution, before the polarization conducted in borax buffers and b) various concentrations of BTA ($6.72 \cdot 10^{-4}$ M, $6.72 \cdot 10^{-5}$ M and $3.36 \cdot 10^{-5}$ M) were added to borax buffers before measurements. In both cases, BTA was found to manifest significant protective properties, but better effect was accomplished by pretreatment. The adsorption of BTA on the copper surface obays the Langmuir's adsorption isotherm.

Keywords: copper, borax buffers, chloride ions, benzotriazole

1. INTRODUCTION

Copper and its alloys have wide range of aplications in many areas of industry such as electronics, for production of wires, sheets, tubes. They are resistant to the influence of atmosfere and many chemicals, however, it is known that in chloride media they are susceptible to corrosion [1, 2]. The mechanism of copper electrodissolution in chloride media has been investigated and it is generally accepted that the anodic dissolution is influenced by chloride concentration independently of pH [3, 4]. At chloride concentrations lower than 1 M, the copper dissolution mechanism can be expressed as [5, 6]:

$$Cu + Cl^- \leftrightarrow CuCl + e^-$$

$$CuCl + Cl^- \rightarrow CuCl_2^-$$

Although only some authors clearly noticed formation of $CuCl_2^-$ it is belived to control the kinetics of anodic dissolution of copper in inhibitor free solutions. At chloride concentrations higher than 1 M complexes $CuCl_3^{2-}$ i $CuCl_4^{3-}$ are formed [4-6]. However, in the alkaline media containing chloride ions the mechanism can be totaly different, so in that case most likely copper oxides are formed [4, 7-9]. The possibility of the copper corrosion prevention has attracted many researchers so until now numerous possible inhibitors have been investigated [10, 11]. Even though non-toxic environmentally friendly inhibitors are more and more studied lately, BTA still has a significant use and it is proved to be efficient for inhibition of copper and its alloys corrosion in alkaline media and in the presence of chloride ions [12-14]. Back in 1963, Dugdale and Cotton [15] observed that benzotriazole, unlike the inhibitors that act only through adsorption, function by true chemical bonding to the metal or metal oxide surface. Benzotriazole (BTA) consists of benzene and triazole ring (Figure 1). The presence of N atoms in molecule enables the bonding between copper surface and benzotriazole [16-24]. Three forms can exist depending on pH value of the solution. In strongly acidic media it has protonated form $BTAH_2^+$, in weakly acidic, neutral and weakly alkaline media its form is BTA, while in strongly alkaline media it is BTA^- [3]. Hope et al. [25] observed that the adsorption of BTA onto the copper surface was reversible at pH levels below 3, and depended upon both solution pH and the applied electrode potential. At lower pH the coordination between Cu and BTA as well as the chemisorption of $BTAH_2^+$ onto the electrode surface occur, whereas at higher pH the surface layer [Cu(I) - BTA] forms. In turn, in acidic media with a high concentration of Cl^- ions and low concentration of BTA, the Cu-BTA films are expected to be soluble [26]. According to the E-pH diagrams for systems containing Cu and BTA, presented by Tromans [9], it may be concluded whether the inhibiting action can be expected. There are opposed oppinions concerning the oxidation state of metal favorable for interaction with BTA, however according to the results of studies BTA is capable for reaction with clean copper surface [3, 27, 28] as well as with Cu_2O and CuO [29-31]. Kosec et al. [32] observed that the morphological characteristics of the surface are smoother in the presence of BTA. This is explained by the formation of the multilayer which composition is described as $Cu/Cu_2O/[Cu(I)-BTA]$.

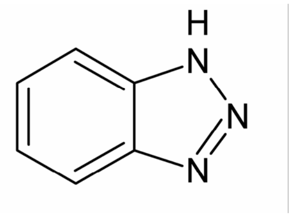

Figure 1. Benzotriazole structure

The layer thickness increases with immersion time and inhibitor concentration [33]. Inhibition efficiency is observed to increase with BTA concentration, whereas at lower BTA concentration activation effect is noticed [14]. This may be attributed to the observation that at lower concentrations inhibitor is chemicaly adsorbed on the electrode surface, while at higher concentrations multilayer film is formed [30].

This paper describes the influence of pH of the solution containing BTA, as well as the influence of simultaneous presence of chloride ions and BTA, on copper corrosion process. It is also presented how the surface coverage degree is influenced by different imersion times of the Cu electrode in the BTA solution, as well as by different BTA concentrations.

2. EXPERIMENTAL PART

2.1. Preparation of the electrode

The working electrode was made of copper wire obtained by upcasting procedure. It was prepared in the following way. The wire was cut and sealed with cold sealing material based on methyl-metacrylat. The working area was 0.49 cm^2. Before each measurement Cu electrode was polished using 1μm grit alumina paste, rinsed with destiled water and dried. The reference electrode was saturated calomel electrode, and the auxiliary one was made of platinum.

2.2. Reagents

Following reagents were used: 0.1 M H_3BO_3; 0.1 M $Na_2B_4O_7$; 0.1 M NaOH. All solutions were made of a. r. grade chemicals.

The borax buffers of specific compositions and pH values (Table 1), were made by mixing the reagents mentioned in the previous paragraph (H_3BO_3; $Na_2B_4O_7$ and NaOH). pH values of all solutions were determined subsequently using the pH-meter MA 5740 (ISKRA-Slovenia).

Table 1. Composition and pH of the borax buffers

	pH				
Amount of reagents for 100cm^3 of borax buffer	8.0	8.7	9.3	10.3	12.3
0.1 M H_3BO_3	95 cm^3	75 cm^3	0	0	0
0.1 M $Na_2B_4O_7$	5 cm^3	25 cm^3	100 cm^3	12.5 cm^3	12.5 cm^3
0.1 M NaOH	0	0	0	24.75 cm^3	35 cm^3
H_2O	0	0	0	62.75 cm^3	52.5 cm^3

Sodium chloride was added to the borax buffers (0.2924 g NaCl in 100 cm^3 of solution) in order to obtain 0.05 M Cl$^-$ solutions.

There were also two series of solutions containing BTA made:

a) Borax buffers containing: $6.72\cdot10^{-4}$ M, $6.72\cdot10^{-5}$ M and $3.36\cdot10^{-5}$ M BTA.
b) Borax buffers containing: $6.72\cdot10^{-4}$ M, $6.72\cdot10^{-5}$ M and $3.36\cdot10^{-5}$ M BTA, with the addition of 0.05 M NaCl.

In order to examine the influence of the immersion time in inhibitor solution on the corrosion of Cu electrode the 0.2 % BTA solution was used.

2.3. Procedure

The apparatus used for electrochemical tests consists of potentiostat directly connected to a computer via an AD card. Applied methods were: measuring of the open circuit potential (OCP) and linear voltammetry. The open circuit potential was determined during 5 min, afterwards the polarization curves were recorded from the open circuit potential up to aproximately 1.0 V vs. SCE. Measurements were performed at scan rate of 10 mV/s. All measurements were conducted at the room temperature. The potential is expressed refering to a saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSION

3.1. The influence of Cu electrode immersion in the benzotriazole solution

3.1.1. Open circuit potential

The behavior of Cu electrode after exposure to $1.68 \cdot 10^{-2}$ M (0.2 %) BTA solution for different time intervals was investigated. Subsequent to the immersion, the open circuit potential was measured for 5 minutes and the polarization was conducted in borax buffers of various pH, with or without chloride ions. The results of these experiments are presented in Tables 2 and 3 and Figures 2 - 6. The results obtained with clean electrode in borax buffers, as well as in chloride ions containing solutions, are provided for comparison.

Table 2. Open circuit potential of copper in borax buffers with and without 0.05 M NaCl, with and without pretreatment in BTA solution

pH	OCP, borax buffers, V vs. SCE	OCP, borax buffers+NaCl, V vs. SCE	OCP, borax buffers, V vs. SCE			OCP, borax buffers+NaCl, V vs. SCE, 15 min
			5 min	15 min	60 min	
8.0	-0.035	-0.174	-0.028	-0.041	-0.027	-0.079
8.7	-0.068	-0.143	-0.062	-0.048	-0.044	-0.079
9.3	-0.120	-0.135	-0.082	-0.070	-0.050	-0.091
10.3	-0.112	-0.098	-0.185	-0.103	-0.179	-0.134
12.3	-0.160	-0.149	-0.161	-0.156	-0.147	-0.159

Detailed examination of the open circuit potential values summarized in Table 2 enables to observe that in borax buffers there is a general trend of OCP being shifted to the negative direction as pH increases, with some discrepancies. However, in the presence of chloride ions the trend is reversed with the exception in pH 12.3 solution. Comparison of the open circuit potential values obtained in the solutions with and without presence of chlorides indicates that the presence of chloride ions renders the open circuit potentials more negative. The same is observed by Milic and Antonijevic [14]. The immersion of the electrode in BTA solution prior to the OCP measurement in borax buffers renders the OCP more positive in pH range 8.0-9.3, and more negative or slightly more positive at higher pH, in solutions either with or without chloride ions. The effect is generally more pronounced as the immersion time increases. The shift of the OCP to more noble values is also observed by other authors and is attributed to the adsorption of BTA on the electrode surface [34]. There is a linear relationship between the open circuit potential and the solution pH, whereby the slopes are, with or without chlorides presence, -0.028 and -0.021 V/pH, respectively.

3.1.2. Anodic polarization behavior of copper in borax buffers with and without chloride ions

According to the studies of the films formed on copper in alkaline solutions, copper electrode surface is covered by oxides providing some protection against corrosion. Feng et al. [35] noticed that as solution pH increases in pH range 6-9 Cu_2O becomes more protective, at pH 10 a thin compact Cu_2O film is formed and spontaneous passivation is observed, at pH 12 and higher copper surface is mostly covered by protective monoclinic CuO layer. However, CuO formed at pH 13 is not protective enough to make copper passive. Minimum thickness is noticed at pH 10, and increases with alkalinity and so does solubility.

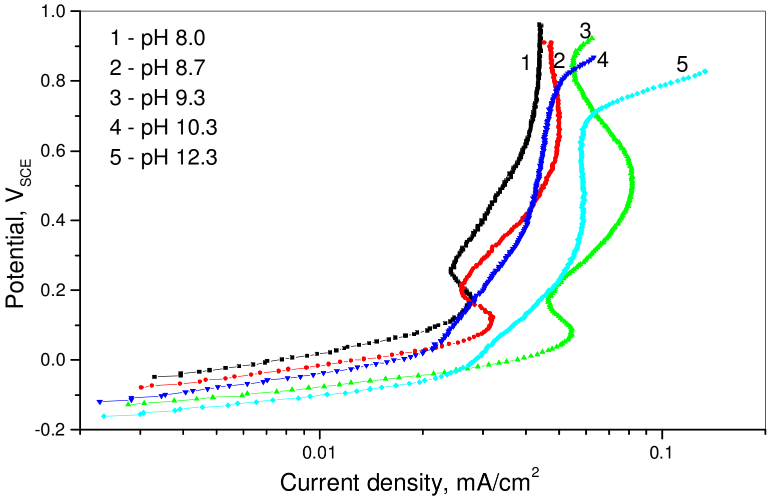

Figure 2. The polarization curves obtained in borax buffers at pH: 1-8.0, 2-8.7, 3-9.3, 4-10.3 and 5-12.3

When the anodic polarization is applied two current peaks can be observed on the anodic polarization curves where the first peak is attributed to the formation of Cu_2O, and the formation of CuO and $Cu(OH)_2$ follows. Similar findings were reported by other authors [1, 3, 8, 31, 36-44].

Copper exhibits passive behavior until potential is reached around 0.8 – 1.0 V vs. SCE when the current starts to increase (Figure 2). Milošev [45] noticed that in borax buffer, pH 9.2, copper is passive and the broad passive range is limited by the oxygen evolution process occurring around 0.8 V vs. SCE. This agrees with some other literature data [8, 43].

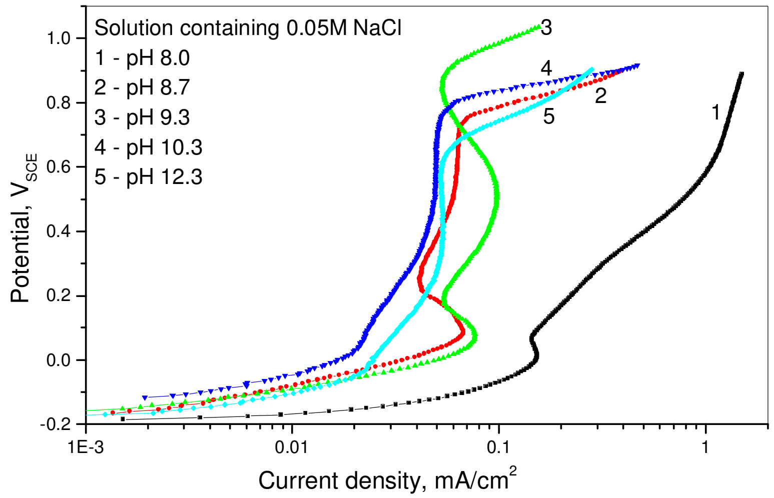

Figure 3. The polarization curves obtained in borax buffers with 0.05 M NaCl at pH: 1-8.0, 2-8.7, 3-9.3, 4-10.3 and 5-12.3

The polarization curves recorded for copper in borax buffers containing 0.05M NaCl, shown in Fig. 3, are similar to those recorded in borax buffer solutions (Fig. 2) but with higher current densities in pH range 8.0-8.7 indicating the activating effect of chloride ions. This is in agreement with the data from other studies [1, 8, 12, 14, 37, 46]. The sudden current density increase at the potential within the passive range in the presence of chloride ions may indicate that passive film suffers localized pitting breakdown [45]. The behavior in the solutions with and without 0.05 M chloride ions is almost the same in solutions pH 9.3 – 12.3, so it can be said that the effect of chlorides diminishes with pH increase. Our findings are in accordance with the results of Modestov et al. [46] who attributed the decrease of the Cl^- ions effect with an increase in pH to the opposite actions of the Cl^- and OH^- ions on the protective properties of the Cu_2O films. The explanation for this kind of behavior may possibly be found in the results of the study of the structure of surface film formed in alkaline solutions in the presence of chloride ions. According to Kunze et al. [47] there is competitive adsorption of OH^- and Cl^- on copper surface. The reaction with OH^- dominates the reaction of Cl^- in alkaline solutions (NaOH pH>11) and the reaction and surface structure are the same.

3.1.3. Anodic polarization behavior of electrode previously exposed to BTA solution

In borax buffers the electrode was tested after being immersed in BTA for 5, 15 and 60 min. Longer the immersion time, lower current density and broader passive area, as can be seen in Figure 4.

However, the difference between 15 and 60 min is not very significant and the satisfactory results are obtained after 15 min pretreatment so in chloride solutions only this time interval is used. The trends are the same as presented in Figure 5 recorded after 15 min exposure in BTA.

Comparison of the curves recorded with clean and pretreated copper electrode (Fig. 2 and 5; 3 and 6) shows that after electrode immersion for 15 min in BTA solution and subsequent polarization, the current densities are considerably lower and the anodic peaks normally present on copper electrode polarization curves are indistinguishable. The same is noticed by Milic and Antonijevic [14]. Considering this, it can be concluded that BTA acts as copper corrosion inhibitor in alkaline media.

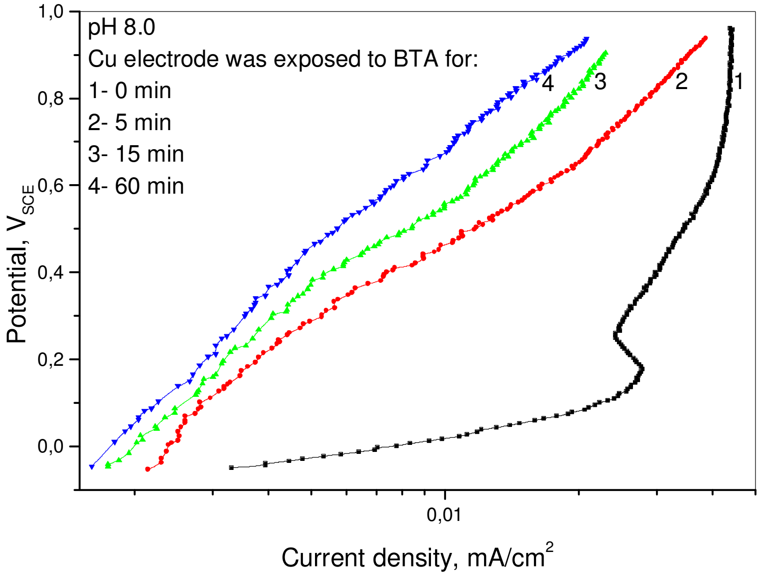

Figure 4. The polarization curves recorded in pH 8.0 borax buffer with the copper electrode previosly exposed to 0.2 % BTA solution for: 1 – 0 min; 2 – 5 min; 3 – 15 min and 4 – 60 min

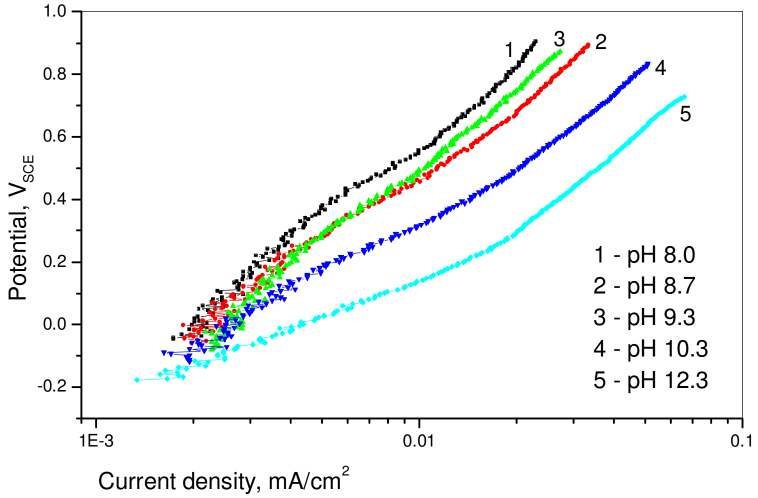

Figure 5. The polarization curves obtained in borax buffers at pH: 1-8.0, 2-8.7, 3-9.3, 4-10.3 and 5-12.3, after the electrode was immersed in BTA for 15 min

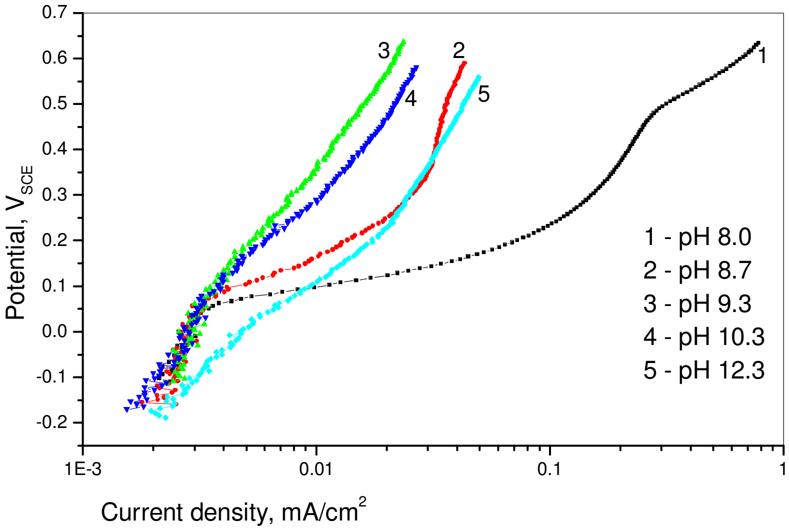

Figure 6. The polarization curves obtained in borax buffers with 0.05 M NaCl at pH: 1-8.0, 2-8.7, 3-9.3, 4-10.3 and 5-12.3, after the electrode was immersed in BTA for 15 min

According to Xue et al. [48] the initial rate of surface film formation reaction in BTA solution is rapid and it slows down after ~20 min and the limiting thickness is reached after 1 h. The explanation of the improved effect with exposure time increase can be found in the earlyer studies regarding the interaction between copper surface, clean or oxide, and BTA in solution [28, 29] and it can be concluded that with the increasing exposure time to inhibitor, the concentration of adsorbed BTA increases and more compact and stable film is formed consisting of (benzotriazolato)copper(I). Higher degree of coverage and improvement of BTA action with longer immersion time is noticed by Milic and Antonijevic [14] and Guilminot et al. [49]. The reaction is faster with clean copper surface than with oxides [28, 48].

As for the effect of solution pH, from the Figure 5 it can be concluded that during polarization in borax buffers in the vicinity of the OCP pH does not have a great influence, but as potential increases the current density increases as pH increase, with the exception at pH 9.3 where the current is lower. In the case of electrode immersion in BTA solution and subsequent polarization in borax buffer containing 0.05 M NaCl (Fig. 6) in pH range 8.0 – 8.7 the passivity occurs in the vicinity of the OCP and in that area pH has no significant effect. The passive range is broader and the currents are lower with pH increase up to 10.3, however further pH increase leads to the narrowing of the passive potential range and current increase. At higher potentials the current density increases with the tendency to equalize with the current recorded during Cu polarization in inhibitor free solutions.

The degree of surface coverage (θ) is calculated using the polarization curves, according to the following equation:

$$\theta = \frac{i - i'}{i}$$

where i - is the current density measured in solution without the prior immersion of electrode in inhibitor and i' - is the current density measured with the electrode previously immersed in inhibitor. The degree of surface coverage, at the potential of 0.050 V vs. SCE, is shown in Table 3. It can be seen that in borax buffers when pH increases in the interval 8.0 - 9.3 the surface coverage degree increases, and at higher pH it decreases, in buffers containing chloride ions surface coverage degree decreases as pH increase. These results can be explained by the fact that CuBTA complex is not stable at high pH, as can be seen from E-pH diagrams for the Cu-BTA-H_2O system [9]. At higher pH the film is thicker and more soluble [48].

Table 3. The surface coverage degree obtained for different immersion times of Cu electrode in BTA

Borax buffer															
pH	8.0			8.7			9.3			10.3			12.3		
Immersion time, min	5	15	60	5	15	60	5	15	60	5	15	60	5	15	60
θ	0.83	0.86	0.86	0.88	0.91	0.91	0.93	0.94	0.94	0.14	0.87	0.72	0.78	0.81	0.88
Borax buffer containing 0.05 M NaCl, immersion time=15 min															
pH	8.0			8.7			9.3			10.3			12.3		
θ	0.98			0.94			0.96			0.86			0.76		

3.2. The influence of BTA concentration

3.2.1. Open circuit potential

The copper electrode behavior during anodic polarization in the presence of various concentrations of BTA ($6.72 \cdot 10^{-4}$ M, $6.72 \cdot 10^{-5}$ M and $3.36 \cdot 10^{-5}$ M) in borax buffers in pH range 8.0-12.3 was investigated. Besides, the effect of simultaneous presence of 0.05 M chloride ions and BTA was investigated. The results are shown in Figures 7 - 10 and Tables 4 and 5.

Table 4. The effect of solution pH and BTA concentration on the open circuit potential

Borax buffer, pH	8.0			8.7			9.3			10.3			12.3		
Concentration BTA $\cdot 10^5$ M	3.36	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2
$-E_{OCP}$, mV_{SCE}	50	69	97	93	116	156	93	123	165	144	141	177	173	182	196
Buffer containing 0.05 M NaCl,pH	8.0			8.7			9.3			10.3			12.3		
Concentration BTA $\cdot 10^5$ M	0.67	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2
$-E_{OCP}$, mV_{SCE}	167*	133	112	138	136	154	126	130	150	117	122	153	155	151	156

It can be seen in Table 4 that the open circuit potential, measured in borax buffers containing BTA, becomes more negative as the BTA concentration increases. Also, increasing solutions pH, at all BTA concentrations, makes the open circuit potential more negative. The open circuit potential increases with time.

In borax buffers containing both chloride ions and BTA, the general correlation between the open circuit potential and pH can not be observed. At pH 8.0 BTA concentration of $0.67 \cdot 10^{-5}$ M was used in order to investigate OCP in the solution with low content of inhibitor. At lower BTA concentrations, the open circuit potential is moved to more positive values in pH range 8.0-9.3, and at pH 10.3 and 12.3 to more negative. At the BTA concentration of $6.72 \cdot 10^{-4}$ M in pH range 8.7-12.3 the open circuit potential becomes more negative and the values for all pH are aproximately equalised. The exception is the open circuit potential obtained at pH 8.0, which is in this case also more positive.

3.2.2. Anodic polarization behavior of copper in borax buffers containing BTA

Data gained from polarization curves recorded in borax buffers containing BTA show that in the presence of BTA anodic current density is lower and peaks are undistinguishable. The effect is more pronounced as the concentration of BTA increases (Figure 7). This is in agreement with the results of the other studies conducted in alkaline solutions [30, 31, 37, 50, 51].

The surface coverage degree values, calculated using the polarization curves, at the potential of 0.050 V vs. SCE, are shown in Table 5.

The important parameter determining the extent of copper corrosion inhibition by BTA is solution pH. It is noticed that with the pH increase form 8.0 up to 9.3 surface coverage degree increases, however further pH increase to 12.3 leads to diminished corrosion inhibition efficiency that is manifested by lower surface coverage degree. According to Metikoš-Huković et al. [44], who studied the inhibition of copper corrosion in 1 M sodium acetate solution in pH range 4-10 in the presence of BTA, the protection increases with increasing inhibitor concentration and solution pH. The dependence of BTA action on pH is explained by the fact that it is a weak acid and the extent of its ionization depends on pH, increases with pH increase. In slightly alkaline solutions the concentration of free BTA^- ions is high and after adsorption they react immediately with copper oxide yielding a complex (CuBTA). Transformation of adsorbed BTA into a Cu(I)-BTA film occurs upon oxidation at higher potentials or upon emersion from BTA solution via a coupled O_2 – induced electrochemical pathway [52]. Qafsaoui et al. [53] characterized the protective films developed on copper by anodic polarization in a borate-buffered solution containing benzotriazole (BTA). It consisted of a thick Cu_2O film, covered by polymeric $[Cu^+BTA^-]_n$ film containing 8 % Cu^+ ions and on Cu_2O areas uncovered by Cu-BTA, CuO appeared. According to the literature data [54] both the Cu_2O surface undergoing corrosion, as well as the adsorption of BTA, occur simultaneously as separate processes. The inhibiting effect is dominating as BTA concentration increases. Nevertheless, the incomplete surface coverage of BTA is sufficient to induce significant changes in the corrosion process of Cu_2O in deionized water, possibly due to the fact that corrosion of the surface occurs on the highest surfaceenergy sites first which most likely participate in adsorption events.

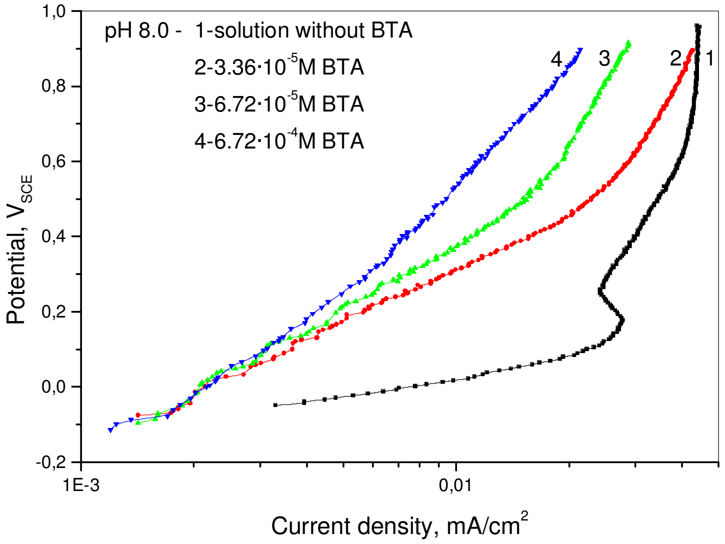

Figure 7. The polarization curves recorded in borax buffers, pH 8.0, 1 – without BTA; 2 – with 3.36·10^{-5} M BTA; 3 – with 6.72·10^{-5} M BTA and 4 – with 6.72·10^{-4} M

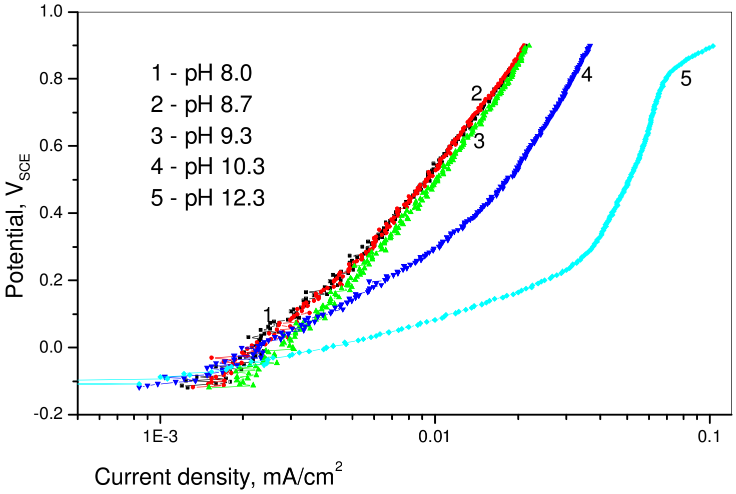

Figure 8. The polarization curves obtained in borax buffers containing 6.72·10^{-4} M BTA at pH: 1-8.0, 2-8.7, 3-9.3, 4-10.3 and 5-12.3

Based on the results obtained from the linear voltammetry presented in polarization curves, shown in Figs. 5 and 8, and Tables 3 and 5, the effects of electrode exposure to BTA solution, before polarization (Fig. 5, Table 3), and the addition of BTA to the solution in which the polarization is performed (Fig. 8, Table 5) can be compared. It can be noticed that better protection is achieved by immersing the electrode in BTA solution. Posibly due to higher BTA concentration and longer exposure time, and also less agresive media for film formation. The higher efficiency of the pretreatment in comparison with the addition of BTA in the solution is confirmed by other studies [14] as well. At lower pH the differences are not distinguished as they are at higher pH, where the addition of BTA to the solution practicaly has no effect what so ever.

3.2.3. Anodic polarization behavior of copper in borax buffers containing BTA and chloride ions

As can be seen in Figure 9. in the presence of lower concentrations of BTA ($3.36{\cdot}10^{-5}$ M and $6.72{\cdot}10^{-5}$ M) and 0.05 M NaCl, at pH 9.3, BTA manifests inhibitive properties only in the vicinity of the open circuit potential. The effects improves when BTA concentration increases to $6.72{\cdot}10^{-4}$ M BTA. The similar results are observed also at pH 8.0 and 8.7. The polarization curves recorded in borax buffers containing both chloride ions and $6.72{\cdot}10^{-4}$ M BTA, are shown in Fig. 10.

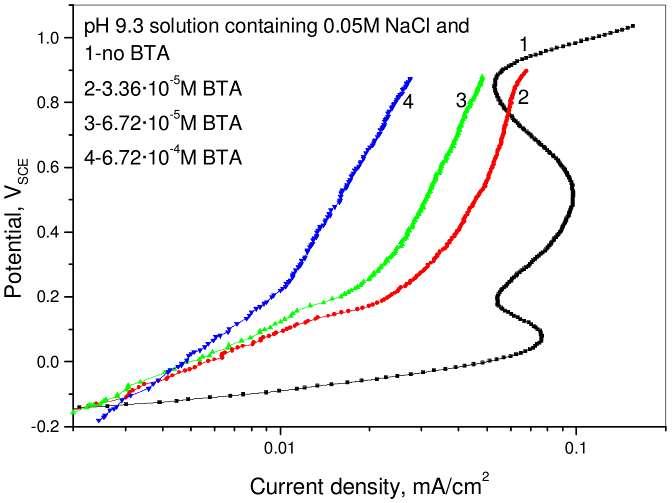

Figure 9. The polarization curves recorded in borax buffers containing 0.05 M NaCl, pH 9.3, 1 – without BTA; 2 – with $3.36{\cdot}10^{-5}$ M BTA; 3 – with $6.72{\cdot}10^{-5}$ M BTA and 4 – with $6.72{\cdot}10^{-4}$ M

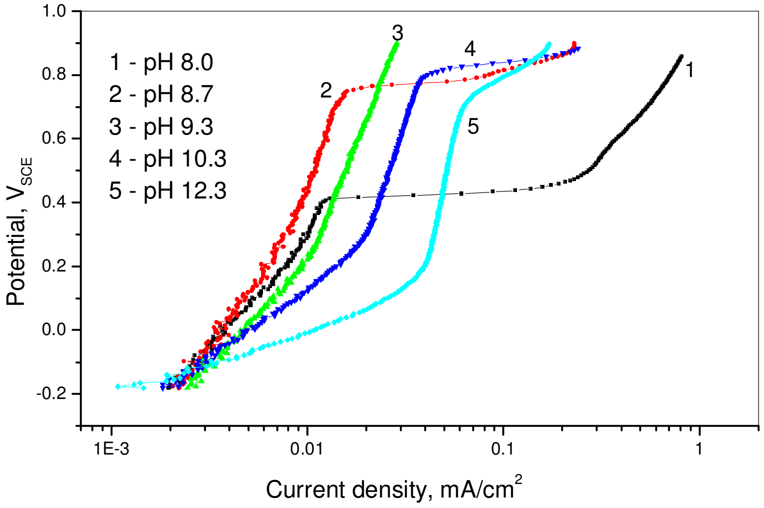

Figure 10. The polarization curves obtained in borax buffers containing 0.05 M NaCl and $6.72{\cdot}10^{-4}$ M BTA at pH: 1-8.0, 2-8.7, 3-9.3, 4-10.3 and 5-12.3

It can be seen that lower current densities and the passivation in wider potential range occur. Lower anodic current density in the presence of BTA is noticed before [14, 32, 55, 56]. According to the numerous studies conducted by different researchers when BTA is present in the solution it adsorbs – chemisorbs on copper surface and forms protective Cu(I)-BTA layer that inhibits copper dissolution [3, 31, 37, 50, 57-61]. It is usually assumed that the surface film has a multi-layer structure Cu/Cu_2O/Cu(I)-BTA [32, 62]. Modestov et al. [26] assume that the most important role of the Cu-BTA layer is in stabilizing the Cu_2O underlayer and maintaining its high resistance. This is achieved by scavenging Cu^+ ions in the Cu-BTA formation reaction and by acting as a low permeable membrane that separates this Cu_2O film from the electrolyte. Another proposal is that the strucure of the layer can be described as Cu_2O mixed with Cu(I)BTA complex within the layer [33]. As for the influence of potential it can be said that at lower potentials BTA is chemisorbed and at higher potentials cuprous ions react with BTA to form Cu(I)-BTA film [63]. The mechanism of complex formation is suggested through the following reactions [57]:

$$Cu_{(s)} + BTAH_{(aq)} = Cu{:}BTAH_{(ads)} + H^+_{(aq)}$$

Where $Cu{:}BTAH_{(ads)}$ refers to BTAH adsorbed on Cu surface. In the presence of oxidants or by anodic polarization it can be oxidized to the complex that has protective properties:

$$Cu{:}BTAH_{ads} = Cu(I)BTA_{(s)} + H^+_{(aq)} + e^-$$

It can be seen that increasing BTA concentration leads to formation of larger amount of protective complex Cu(I)BTA. The improvement of inhibition efficiency with BTA concentration is confirmed in our experiments and also in literature data [33, 56]. Chen et al. [64] found that in 0.5 M NaCl solution pH 9 the growth kinetics changes when BTA concentration increase, from parabolic law to logarithmic law at the critical concentration of BTA 0.17 mM. It is speculated that the film with a different growth kinetics also has a different structure. Film growing as logarithmic law is more complete, thight and polymerized and has more protection. Additionaly the presence of CuO in the film decreases the thermodynamic stability of Cu and hence the inhibition ability increases with the concentration of BTA. Films formed in the presence of low and high concentration of BTA on Cu surface are Cu/Cu^0-Cu_2O/CuO-Cu(I)BTA and Cu/Cu^0-Cu_2O-Cu(I)BTA, respectively. Similar is concluded by Finšgar et al. [65].

With increase of pH, in the presence of chlorides, and at the highest tested BTA concentration ($6.72{\cdot}10^{-4}$ M) the inhibitive action of BTA decreases, which is also indicated by the surface coverage degree values calculated based on polarization curves, at potential of 0.050 V vs. SCE, presented in Table 5. However, the potential at which the rapid current density increas appears becomes more positive with pH increase up to 9.3, and afterwards it happens at less positive potentials. Fenelon and Breslin [62] studied the effect of BTA on copper corrosion in NaCl solutions pH 3.0 - 9.0. In all cases BTA induced passivation effect due to prevention of thermodynamically stable chloride-containing species formation. According to the data colected in our tests and by comparison of them with thermodynamic data presented in E-pH diagram for systems Cu-H_2O-BTA i Cu-H_2O-BTA-Cl constructed by Tromans [9] it is found that at pH 8.0, 8.7, 9.3 and 10.3, in the presence of BTA (concentration of $6.72 \cdot 10^{-4}$M) and chlorides, mostly CuBTA layer is formed on Cu surface, which is the reason why there are no distinct anodic peaks on the polarization curves corresponding to formation of Cu_2O i CuO. The polarization curves recorded at pH 12.3 show that BTA does not act well as an inhibitor in that case since in this area the protective film CuBTA does not form.

The effects of immersion of Cu electrode in BTA solution, before polarization, and the addition of BTA to the solution in which the polarization is conducted and that contain chloride ions, can be compared based on polarization curves shown in Figs. 6 and 10. It can be observed that wider passive region appears at pH 8.0, 8.7 and 9.3 when BTA is added to the solution, but the surface coverage is somewhat lower. At higher pH immersion of Cu electrode in BTA solution is more effective, whereby the protective film is formed, before the polarization in tested solutions.

Table 5. The copper electrode surface coverage degree obtained for different BTA concentrations, calculated using the data gathered by linear voltammetry conducted in borax buffers containing BTA

The surface coverage degree, $\theta=(i-i')/i$															
pH	8.0			8.7			9.3			10.3			12.3		
Concentration of $BTA \cdot 10^5$ M	3.36	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2	3.36	6.72	67.2
Borax buffer	0.82	0.82	0.83	0.88	0.87	0.87	0.91	0.92	0.92	0.67	0.76	0.80	-	-	0.44
Borax buffer containing 0.05 M NaCl	-	0.16	0.98	0.31	0.79	0.93	0.89	0.91	0.92	-	0.57	0.68	-	-	0.39

3.3. The adsorption isotherm

The mechanism of BTA adsorption on the copper surface is investigated using the Lengmuirs isotherm. The main equation is:

$$\frac{\theta}{1-\theta} = \mathrm{AC}\exp\left(\frac{-\Delta \mathrm{G}}{\mathrm{RT}}\right)=\mathrm{KC}$$

Where K - is the constant of adsorption process and ΔG - is adsorption energy, C - is concentration of BTA (mol/dm^3) and θ - is the degree of surface coverage. The equation can be expresed in form:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Relation between the adsorption constant and the adsorption energy is:

$$K = \frac{1}{55.55}\exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$

It leads to:

$$\ln K - \ln\frac{1}{55.55} = -\frac{\Delta G}{RT}$$

$$-\Delta G = (\ln K - \ln\frac{1}{55.55})RT$$

where R is the universal gas constant (8.314 J/mol), and T is the thermodynamic temperature (293 K). Based on the surface coverage degree (Table 5) and the corresponding BTA concentrations the correlation between C/θ and C is investigated. Fig. 11 shows the correlation between C/θ and BTA concentration in pH 9.3 borax buffer. It can be seen that there is a linear relation indicating that the adsorption of BTA on copper surface obays the Langmuirs' isotherm. The same is observed by other studies [14, 30, 32, 54]. For all other pH values, for solutions containig only BTA as well as for solutions containing both BTA and chloride ions, similar linear relations between C/θ and C are obtained. The adsorption energies are calculated and the values are presented in Table 6.

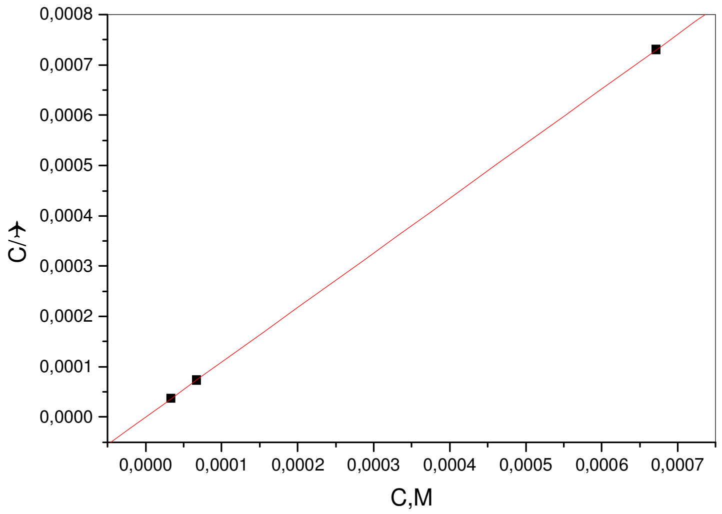

Figure 11. The Langmiurs adsorption isotherm obtained for the borax buffer pH 9.3

Table 6. The adsorption energy values

pH - borax buffer	8.0	8.7	9.3	10.3	12.3
ΔG, kJ/mol	-44.01	-	-47.09	-38.75	-
pH - borax buffer containing 0.05 M NaCl	8.0	8.7	9.3	10.3	12.3
ΔG, kJ/mol	-	-34.06	-43.20	-	-

The adsorption energies have values in range from -34 to -47 kJ/mol which indicate that the first step of inhibitor action is chemisorption on copper surface. The other authors came to the same conclusion [3, 14, 30, 31, 34, 37, 57]. The chemisorption may be followed by the polymer Cu(I)BTA film formation and there is an equilibrium between the adsorption and complex formation [30]:

$$n(BTA\text{-}H)_{ads} + nCu \leftrightarrow [Cu(BTA)]_n + nH^+ + ne^-$$

indicating that at higher pH the formation of complex is promoted. Protective film formed on copper electrode in the presence of BTA acts as a physical barrier preventing the aggressive species from reaching the copper surface. When the time is short or the BTA concentration is low it is possible that there are places on the surface where the protective film is not formed and the metal dissolves at those spots. Longer time of electrode immersion or the higher BTA concentration allows the formation of compact protective CuBTA film, which prevents metal corrosion.

4. CONCLUSIONS

1. The current densities are considerably lower and the anodic peaks normally present on copper electrode polarization curves are indistinguishable when the electrode is exposed to BTA solution prior to the polarization in borax buffers with or without Cl^- ions.
2. As for the effect of solution pH, in borax buffers in the vicinity of the OCP pH does not have a great influence, but as potential increases the current density increases as pH increase.
3. In borax buffer containing 0.05 M NaCl in pH range 8.0 – 8.7 the passivity occurs in the vicinity of the OCP and in that area pH has no significant effect. The passive range is broader and the currents are lower with pH increase up to 10.3, however further pH increase leads to the narrowing of the passive potential range and current increase.
4. In borax buffers when pH increases in the interval 8.0 - 9.3 the surface coverage degree increases, and at higher pH it decreases, in buffers containing chloride ions surface coverage degree decreases as pH increase.
5. Data gained from polarization curves recorded in borax buffers containing BTA show that in the presence of BTA anodic current density is lower and peaks are undistinguishable. The effect is more pronounced as the concentration of BTA increases.
6. With the pH increase form 8.0 up to 9.3 surface coverage degree increases, however further pH increase to 12.3 leads to diminished corrosion inhibition efficiency that is manifested by lower surface coverage degree.
7. Better protection is achieved by immersing the electrode in BTA solution. At lower pH the differences are not distinguished as they are at higher pH, where the addition of BTA to the solution practicaly has no effect what so ever.
8. The surface coverage degree value, calculated using the polarization curves, at the potential of 0.050 V vs. SCE, increases with pH up to 9.3, while at higher pH it decreases.
9. In the presence of lower BTA concentrations ($3.36\cdot10^{-5}$ M and $6.72\cdot10^{-5}$ M) and 0.05 M NaCl, at pH 8.0, 8.7 and 9.3, BTA manifests inhibitive properties only in the vicinity of the open

circuit potential. In borax buffers containing $6.72 \cdot 10^{-4}$ M BTA, lower current densities and the passivation in wider potential range occur.

10. With increase of pH, in the presence of chlorides the inhibitive action of BTA decreases. However, the potential at which the rapid current density increas appears becomes more positive with pH increase up to 9.3, and afterwards it happens at less positive potentials.
11. Wider passive region appears at pH 8.0, 8.7 and 9.3 when BTA is added to the solution, but the surface coverage is somewhat lower. At higher pH immersion of Cu electrode in BTA solution is more effective.
12. BTA chemically adsorbs on copper surface according to Lengmuirs' isotherm.

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