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Influence of pH and Chlorides on Electrochemical Behavior of Brass in Presence of Benzotriazole

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This paper describes an investigation of the corrosion behavior of Cu37Zn brass in borate buffer solutions at various pH, in the presence of benzotriazole, with and without the addition of chloride ions. The values of anodic current densities are considerably smaller in borate buffer solutions with the addition of benzotriazole compared with those in the inhibitor-free solution. The study analyses the electrochemical behavior of Cu37Zn brass after various times of brass exposure to solution of benzotriazole, as well as its' behavior in solution of benzotriazole of various concentrations.

Keywords: Brass, Benzotriazole, Chloride ions, Polarization

1. INTRODUCTION

Copper and its alloys are widely used in industry because of their good resistance to corrosion, in cooling water systems, for shipboard condensers, power plant condensers and petrochemical heat exchangers. Brass is very interesting for many scientists, because of its' great industrial importance. Behavior of brass was studied in seawater [1,2], NaCl [3-8], H_2SO_4 [9, 10], HNO_3 [11, 12], borate buffer [13-15], sodium tetraborate [16]. Organic compounds from different groups showed inhibition properties. The most representative compounds were from following groups: tetrazole compounds [9, 17, 18], terdentate ligands [13], triazole compounds [12,19-21], benzotriazole and benzotriazole derivates [1, 5, 6, 22-26]. Anxiety for environment causes need for environmentally-friendly inhibitors such as purine [27, 28], adenine [28, 29], caffeine [30], aminoacides [31-35].

Benzotriazole (BTA) was heedful study like inhibitor, and it is one of the best inhibitor for copper and its alloys in different solutions [6, 24, 36], and at different pH [37] and it is modifying the electrochemical dissolution of a zinc rich copper alloy [36]. At the present time, it is still discussed when the inhibitive film is formed as Cu(I)BTA complex, $[Cu(BTA)]_n$, adsorbed BTA film or as a BTA polymer structure [38]. The interaction of BTA with the surfaces of copper and its alloys is a subject of considerable importance in connection with its use as a corrosion inhibitor [39], and two mechanisms for inhibition have been proposed. According to the first mechanism Cu(I)BTA polymeric film was formed on the electrode surface [40, 41] or adsorbed layer of BTA on the metal surface was formed according to the second mechanism [23, 42, 43]. Also, it must be mentioned that change in the pH leads to change in the corrosion mechanism [37]. Dominant species of BTA depend on solution pH, so in alkaline solutions (pH>8) BTA^- species are dominant whereas in the acidic solutions (pH<1) $BTAH^+$ species are dominant [38, 40]. In the solutions where pH is between 2-8 neutral molecule of BTA is stable [38]. Electrochemical behavior of copper and copper alloys in chloride containing solution with BTA was extensively studied [22, 36]. Despite these investigations there are relatively little information on the mode of action of BTA in the corrosion inhibition of copper-zinc alloys.

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 corrosion process at brass surface. It is also presented how the surface coverage degree is influenced by different imersion times of the Cu37Zn electrode in the BTA solution, as well as by different BTA concentrations.

2. EXPERIMENTAL PART

The working electrode was made of Cu37Zn brass with an area of $0.49cm^2$. The electrode was prepared from a brass wire (ø=0.79cm), it was cut and sealed with epoxy resin. Before each measurement, the working electrode was polished using 1μm grit alumina paste, rinsed with distilled water and dried. The reference electrode was saturated calomel electrode (SCE), and the auxiliary one was made of platinum. The apparatus used for electrochemical measurements holds potentiostat directly connected to a computer via an AD card.

Following reagents were used: 0.1M solution of H_3BO_3, 0.1M solution of $Na_2B_4O_7$, 0.1M solution of NaOH and $1.68\cdot10^{-2}$M solution of BTA. All solutions were made of a.r. grade chemicals.

Composition and pH of initial solutions are presented in Table 1. The initial solutions were made by mixing the solutions mentioned above (0.1M H_3BO_3, 0.1M $Na_2B_4O_7$ and 0.1M NaOH). pH values of solutions were measured using pH-meter MA5740 ISKRA-Slovenia

Table 1. Composition and pH of initial solutions

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

NaCl (0.2924g NaCl in $100cm^3$) was added in initial solution. Concentration of chloride ions was 0.05M. Also, two series of BTA solutions were made:

a) The suitable amount of BTA solution was added in initial solutions. The concentrations of BTA solutions were: $6.72\cdot10^{-4}$, $6.72\cdot10^{-5}$ and $3.36\cdot10^{-5}$M.

b) NaCl was added in the solutions with BTA. Concentration of NaCl was 0.05M.

The methods used were: measuring of the open circuit potential and linear voltammetry. The linear voltammograms were recorded starting from the corrosion potential to 1.0V vs. SCE. Measurements were conducted at a scan rate of $10mVs^{-1}$. All measures were done at the room temperature.

The electrochemical behavior of Cu37Zn brass in borate buffer solutions in the presence of chloride ions and benzotriazole was investigated in the following way:

a) The electrode was immersed for a certain time in a 0.2% BTA solution (5, 15 and 60min), then rinsed with distilled water and immersed into the borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3) in which polarization was immediately performed.
b) The electrode was immersed for a 15min in a 0.2% BTA solution, then rinsed with distilled water and immersed into the borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3) containing chloride ions ($0.05moldm^{-3}$) in which polarization was performed immediately.
c) The electrode was immersed in borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3 and 12.3) containing different concentrations of BTA ($3.36\cdot10^{-5}$, $6.72\cdot10^{-5}$ and $6.72\cdot10^{-4}moldm^{-3}$) where polarization was performed.
d) The electrode was immersed in a borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3) containing various concentrations of BTA and chloride ions in which polarization was performed immediately.

3. RESULTS AND DISCUSSION

3.1. The influence of Cu37Zn electrode immersion in the benzotriazole solution

3.1.1. Open circuit potential

Open circuit potential (OCP) of Cu37Zn was recorded in borate buffer solution of various pH (8.0, 8.7, 9.3, 10.3, 12.3) after previous immersion in 0.2% BTA solution (Tab. 2). It was found that OCP become more negative when pH increases.

Table 2. Open circuit potential as a function of pH in borate buffer solutions of various pH with different immersion time (5, 15, 60min) in 0.2% BTA solution

Open circuit potential of brass electrode in borate buffer solutions of various pH after exposure in 0.2% BTA solution, V vs. SCE			
pH	5 min	15 min	60 min
8.0	-0.126	-0.125	-0.129
8.7	-0.150	-0.160	-0.159
9.3	-0.167	-0.178	-0.170
10.3	-0.238	-0.224	-0.220
12.3	-0.248	-0.243	-0.243

Open circuit potential had approximately same values when the electrode was immersed in BTA solution for 5, 15 and 60min. (Tab.2.). These show that passive film which was formed on brass surface was of the same composition without considering immersion time. Brass surface was covered with this layer after 5min.

3.1.2. Polarization measurements in borax buffer solution with and without chloride ions

The behavior of brass electrode after different immersion time (5, 15 and 60min) in 0.2 % BTA solution was investigated. Polarization curves showed that current density depends on immersion time in 0.2% BTA solution and it is obvious that with increase of immersion time, the current density decrease (Fig. 1.). Generally current density had the lowest values in the whole potential region when the brass electrode was immersed 60min in 0.2% BTA solution. The passive layer on brass surface was thinner when electrode was immersed in BTA solution for shorter time (5 and 15min). Metikos-Hukovic et al. [44] found that film thickness increase by increasing the BTA concentration and immersion time. Xue et al. [45] found that initial rate of surface film formation was rapid and slowed down after 20min. Maximal thickness was reached after 1h.

Protective property of BTA can be explained by formation of stable and insoluble protective layer which contains BTA [12, 24]. The protective film is composed of multilayer of the $[Cu(I)BTA]_n$ complex even though $[Zn_2BTA_4]_n$ complex can be present [46]. Benzotriazole could react with copper atom to form a benzotriazole copper complex [39] when electrode was immersed in a BTA solution [47].

Youda et al. [48] have suggested that the adsorption and the complex formation are in equilibrium

$$n(BTA)_{ads} + nCu = [Cu(BTA)]_n + nH^+ + ne^-$$

and this shows that increasing pH value favors the complex formation. Formation of the surface film has been accomplished after the adsorption of BTA on the electrode surface [49].

The relation between current density and pH was studied, with immersion of brass electrode for 60min in the 0.2% BTA solution, and the results are presented on Fig. 2. It is easy to observe that current density increase when pH increases. The same was observed after 5 and 15min immersion of electrode in the BTA solution. This results show that BTA have better protective effect at lower pH values, which is probably a consequence of weak binding of BTA on the brass surface at higher pH. BTA adsorption was lower on brass surface when concentration of OH^- ions increased, especially in pH interval from 10.3 to 12.3. This is probably consequence of formation of coppers' oxides (Cu_2O, CuO) and hydroxides ($CuOH$, $Cu(OH)_2$) on the brass surface in the alkaline solution. Cu_2O film was dominant on the electrode surface at pH 10 but at higher pH CuO was dominant [37]. Copper can be oxidized to Cu(I)hydroxide according to [50]:

$$Cu + OH^- = CuOH + e^-$$

Also, it is important to mention that the major Cu(II) species is CuO because it is more stable thermodynamically than $Cu(OH)_2$ [37] due to reaction [50]:

$$Cu(OH)_2 = CuO + H_2O$$

Composition of the passive film for brass is $ZnO/Cu_2O/Cu(OH)_2$ and that composition has effect on the corrosion resistance [51].

Table 3 contains values of the degree of coverage and it was calculated according to the following equation:

$$\theta\,[\%] = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100$$

Where I_{corr} is the current density in the inhibitor-free solution and $I_{corr(inh)}$ is the current density in the presence of the inhibitor.

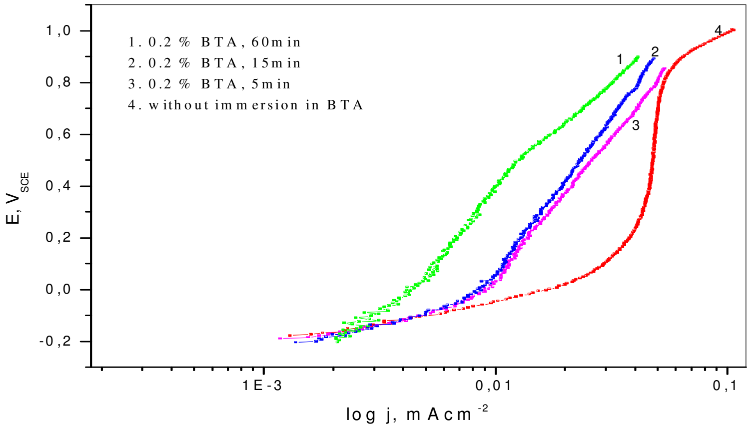

Figure 1. Polarization curves of Cu37Zn brass in borate buffer solution at pH 9.3. The electrode was immersed in a 0.2% BTA solution for a varied time period (5, 15 and 60min.), rinsed with distilled water and immersed into a borate buffer solution (pH 9.3) in which polarization was performed at scan rate $10 mVs^{-1}$

Table 3. The degree of coverage as a function of immersion time in 0.2% BTA solution at various pH at potential 0.05V vs. SCE

θ[%]					
t[min]	pH 8.0	pH 8.7	pH 9.3	pH 10.3	pH 12.3
5	67.59	75.92	78.08	-	14.75
15	67.46	82.22	79.86	44.61	8.81
60	83.13	85.44	89.2	54.55	30.84

From table 3 it is seen that surface coverage considerably decrease at higher pH (10.3 and 12.3) which is a result of a low BTA absorption on the brass surface. Generally speaking, the degree of coverage increases with increase of immersion time in 0.2% BTA solution. The probable reason for this is the formation of a thicker protective film [52,53], and that film which grows with immersion time, according to some paper, didn't influence the corrosion mechanism but physically blocks the electrode surface [38].

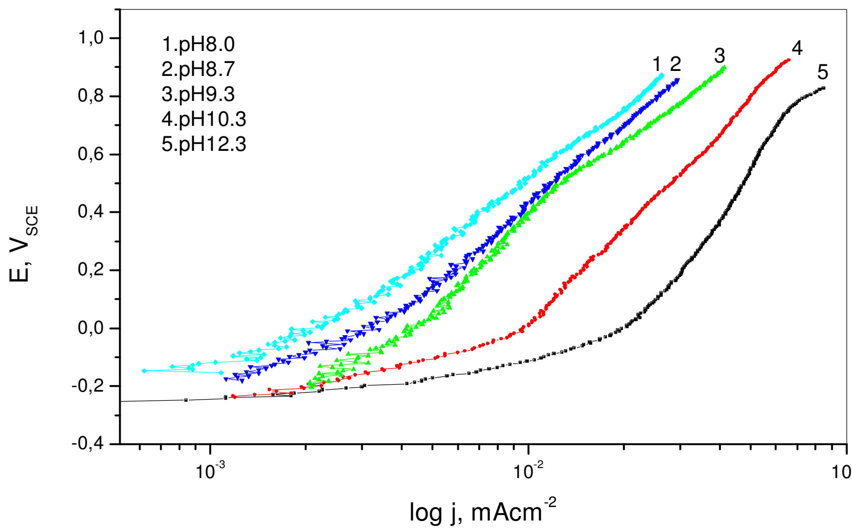

Figure 2. Polarization curves of Cu37Zn brass in borate buffer solutions of various pH (8.0, 8.7, 9.3, 10.3, 12.3). The electrode was immersed in 0.2% BTA solution for 60min, rinsed with distilled water and carried into a borate buffer solution in which polarization was done at scan rate $10mVs^{-1}$

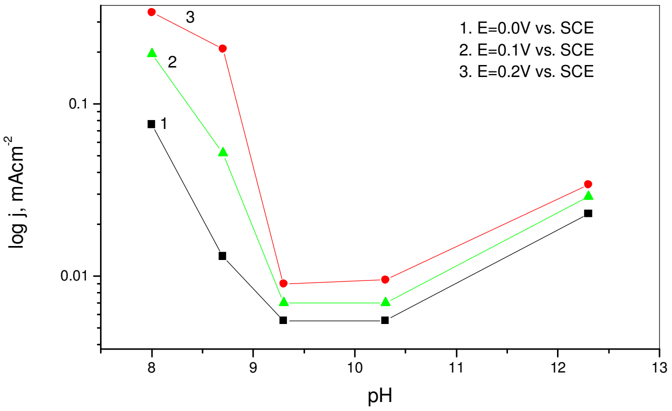

Figure 3. Current density as a function of pH in a borate buffer solution containing chloride ions ($0.05moldm^{-3}$) at potentials 0.0, 0.1 and 0.2V vs. SCE

BTA influence on brass behavior was observed in borate buffer solution of various pH with the addition of NaCl ($C_{NaCl}=0.05moldm^{-3}$). Electrode was immersed 15min in 0.2 % BTA solution and after that polarization measurement was performed and results are presented in table 4. The degree of coverage was calculated at 0.05V vs. SCE and the highest value was at pH 9.3 (Tab. 4). It is easy to see that current density increase with increasing potential at all tested pH. It is very important to mention that protective film in the vicinity of the corrosion potential is resistant to the effect of chloride ions at all pH. Antonijevic et al. [52] came to the similar results in borate buffer solutions with different concentration of Cl$^-$ at pH 10. Current density decrease with pH increase from 8.0 to 9.3, afterwards it has constant values at 9.3 and 10.3 and at 12.3 increase at all observed potentials (Tab. 4). The current density had the highest values at lower pH and at higher potential (Fig. 3).

Table 4. Current density and the degree of coverage in borate buffer solution with addition of NaCl at various pH. Electrode was immersed 15min in 0.2% BTA solution

θ [%]	pH					
/	8.0	E [V_{SCE}]	0.0	0.05	0.1	0.2
		j [$mAcm^{-2}$]	0.076	0.13	0.19	0.34
36.76	8.7	E [V_{SCE}]	0.0	0.05	0.1	0.2
		j [$mAcm^{-2}$]	0.012	0.018	0.05	0.20
88.4	9.3	E [V_{SCE}]	0.0	0.05	0.1	0.2
		j [$mAcm^{-2}$]	0.005	0.006	0.007	0.009
70.5	10.3	E [V_{SCE}]	0.0	0.05	0.1	0.2
		j [$mAcm^{-2}$]	0.005	0.006	0.007	0.009
35.95	12.3	E [V_{SCE}]	0.0	0.05	0.1	0.2
		j [$mAcm^{-2}$]	0.022	0.026	0.029	0.034

Table 5. Open circuit potential in the borax buffer solution with various concentration of BTA, with and without NaCl at various pH

Open circuit potential in the borax buffer solution with addition of BTA															
C_{BTA}	$3.36\cdot10^{-5}$ moldm^{-3}					$6.72\cdot10^{-5}$ moldm^{-3}					$6.72\cdot10^{-4}$ moldm^{-3}				
pH	8.0	8.7	9.3	10.3	12.3	8.0	8.7	9.3	10.3	12.3	8.0	8.7	9.3	10.3	12.3
E[V_{SCE}]	-0.082	-0.126	-0.156	-0.173	-0.208	-0.135	-0.184	-0.225	-0.183	-0.206	-0.164	-0.195	-0.262	-0.22	-0.267
Open circuit potential in the borax buffer solution with addition of BTA and 0.05M NaCl															
C_{BTA}	$3.36\cdot10^{-5}$ moldm^{-3}					$6.72\cdot10^{-5}$ moldm^{-3}					$6.72\cdot10^{-4}$ moldm^{-3}				
pH	8.0	8.7	9.3	10.3	12.3	8.0	8.7	9.3	10.3	12.3	8.0	8.7	9.3	10.3	12.3
E[V_{SCE}]	-0.146	-0.148	-0.174	-0.214	-0.217	-0.144	-0.19	-0.196	-0.218	-0.231	-0.263	-0.198	-0.28	-0.231	-0.265

3.2. Behavior of Cu37Zn brass in borate buffer solutions in the presence of various concentrations of BTA

3.2.1. Open circuit potential

Influence of BTA on electrochemical behavior of Cu37Zn brass was observed in borate buffer solutions with addition of various concentrations of BTA ($3.36\cdot10^{-5}$, $6.72\cdot10^{-5}$ and $6.72\cdot10^{-4}$moldm^{-3}). Open circuit potential was measured and results showed that OCP becomes more negative when concentration of BTA increases at all pH. Generally, pH also had influence on OCP, make it more negative (Tab. 5) [22]. Open circuit potential in borax buffer solutions with addition of BTA ($6.72\cdot10^{-4}$moldm^{-3}) and NaCl had similar values like in solution without NaCl except at pH 8.0 when OCP had more negative values in the borax buffer solution with NaCl. In the borax buffer solution with lower concentration of BTA ($3.36\cdot10^{-5}$ and $6.72\cdot10^{-5}$moldm^{-3}) open circuit potential had more positive values in comparison with solutions containing NaCl at the same pH (Tab. 5).

3.2.2. Polarization measurements in borax buffer solution containing BTA without chloride ions

The electrochemical behavior of Cu37Zn brass in borate buffer solutions of various pH in the presence of various concentrations of BTA is shown in Fig. 4. Results presented on this figure showed that change of BTA concentration has influence on current density at all observed pH, except at pH 12.3. Generally, current density decrease when BTA concentration increase [52, 54], but at pH 12.3 presence of BTA didn't show decrease of current density. BTA solution of higher concentration ($6.72\cdot10^{-5}$ and $6.72\cdot10^{-4}$moldm^{-3}) shows good inhibition properties at pH 8.0-9.3.

Table 6. The degree of coverage as a function of BTA solutions of various concentration, at various pH and at potential 0.05V vs. SCE

	θ[%]				
C_{BTA} [moldm^{-3}]	pH 8.0	pH 8.7	pH 9.3	pH 10.3	pH 12.3
$3.36\cdot10^{-5}$	-	24.86	80.11	39.18	9.42
$6.72\cdot10^{-5}$	69.99	82.45	89.12	51.8	-
$6.72\cdot10^{-4}$	84.46	84.52	89.04	79.20	11.69

Aramaki et al. [55] found that formation of protective complex polymer in the solution with BTA was preferenced at high pH values. This observation is in agreement with results presented in table 6. Peaks which correspondent to the formation of copper oxides weren't observed on curves, and that confirm inhibiting effect of BTA. Antonijević et al. [52] came to the similar results in the previous work. Degree of coverage increase when BTA concentration and pH increase in the interval from 8.0 to 9.3. At higher pH (10.3 and 12.3) θ decrease when pH increase (Tab. 6.). This is probably associated with stability of protective film and dominant oxidation state of copper [52].

Metikoš-Huković et al. [54] and Feng et al. [37] claim that oxidation state of copper is associated with pH values, so at pH around 10 Cu(I) is stable but at higher pH Cu(II) form is dominant. On the basis of results presented in tab. 6. it can be seen that degree of coverage depends on BTA concentration [54, 56]. Furthermore, the multilayer structure on the electrode surface depends on BTA concentration [57]. The addition of BTA modified the surface film, forming protective $[Cu(I)BTA]_n$ film [10,12,24,52]. In alkaline solution, concentration of BTA^- is relatively high and it reacts with copper forming complex compound [54], but protective property of BTA become weak at higher pH (Fig. 5) probably because of OH^- ions adsorb on brass surface.

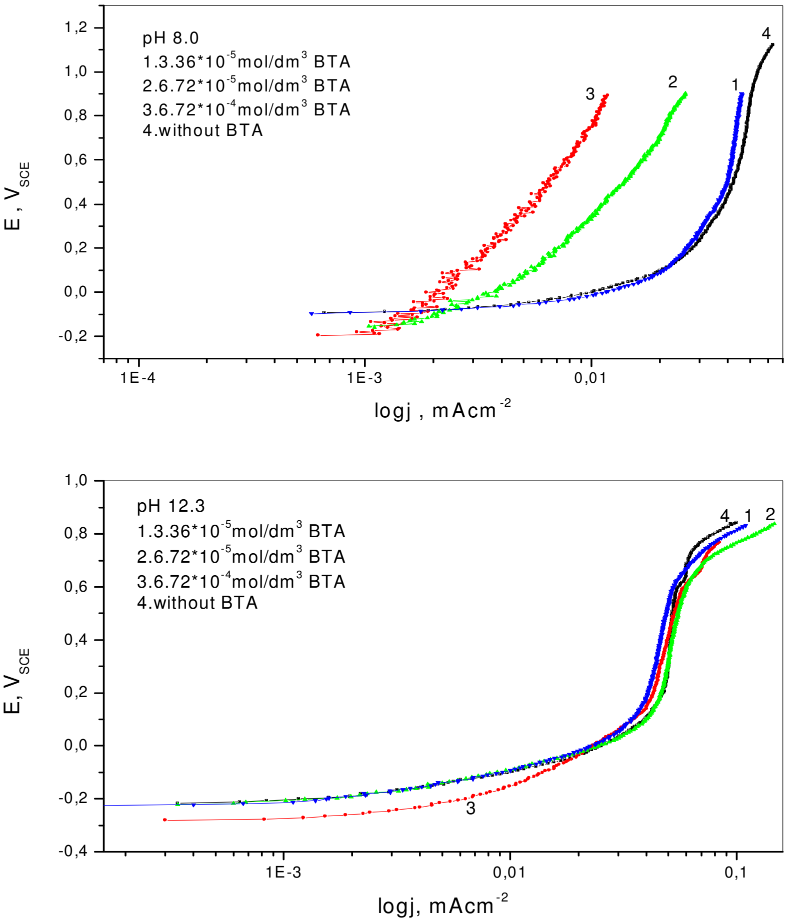

Figure 4. Polarization curves of Cu37Zn brass in borate buffer solutions at pH 8.0 and 12.3 in presence of BTA solutions of various concentrations ($3.36\cdot10^{-5}$, $6.72\cdot10^{-5}$, $6.72\cdot10^{-4}$moldm^{-3}). The polarization was done immediately after the electrode immersion in the solutions at scan rate 10mVs^{-1}

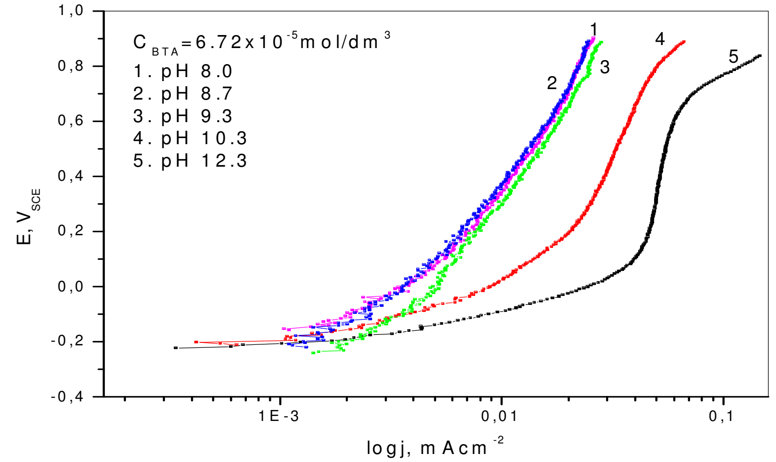

Figure 5. Polarization curves of Cu37Zn in borate buffer solution with addition of $6.72\cdot10^{-5}$M BTA at various pH (8.0; 8.7; 9.3; 10.3; 12.3). The polarization was done immediately after the electrode immersion in the solutions, at scan rate 10mVs^{-1}

3.2.3. Polarization measurements in borax buffer solution with addition of BTA and chloride ions

Influence of various concentrations of BTA was observed in borate buffer solutions of various pH with addition of chloride ions (C_{NaCl}=0.05moldm^{-3}). Concentrations of BTA solutions were as in previous experiments. Data gained from polarization curves point to that the lowest concentration of BTA (3.36·10^{-5}moldm^{-3}) didn't had influence on current density decreasing. Effects of BTA on the anodic current density increase with increasing BTA concentration in the borax buffer solution at pH 9.3 (Fig. 6). Similar results were observed at pH 8.7 but at pH 8.0 only the highest concentration of BTA manifested inhibitive properties. Results obtained on Figure 6 point to that BTA didn't show decrease of current density at pH 12.3, and that was like in the solution without chloride ions.

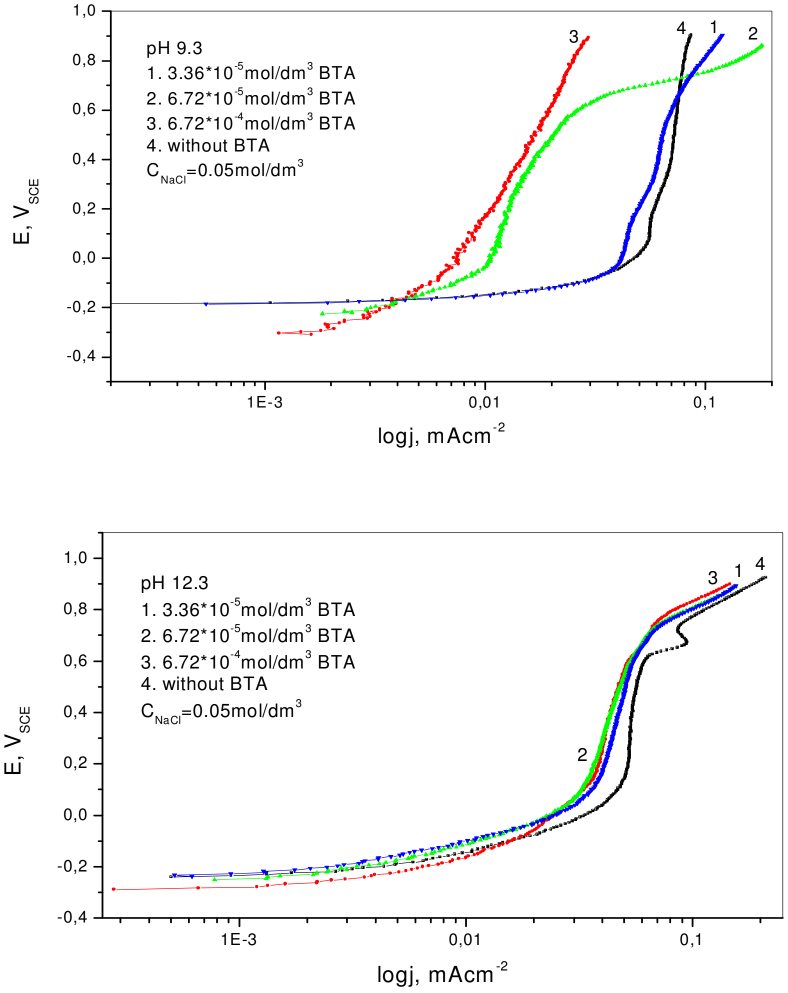

Figure 6. Polarization curves of Cu37Zn brass in borate buffer solutions at pH 8.0 and 12.3 in presence of BTA solutions of various concentration (3.36·10^{-5}, 6.72·10^{-5}, 6.72·10^{-4}moldm^{-3}) with additional of chloride ions (C_{NaCl}=0.05moldm^{-3}). The polarization was done immediately after the electrode immersion in the solutions, at scan rate 10mVs^{-1}

Besides, some other studies had shown that BTA concentration had influence on anodic current density [6, 16, 39, 57, 58] and that BTA achieve passivation of electrode surface [39]. The polarization curves recorded in borax buffers containing both chloride ions and $6.72\cdot10^{-5}$moldm^{-3} BTA, are shown in Figure 7. Result acquired from Figure 7. lead to conclusion that pH had an effect on anodic current densities decrease. Degree of coverage reveal that BTA has good inhibitive properties in the pH range from 8.0 to 9.3 (Tab. 7.), and that is in the agreement with current density decreasing in the same pH interval (Fig. 7.). Also, results presented in the Table 7. lead to inference that in the strongly alkaline solution (pH>10) inhibitive action of BTA decline.

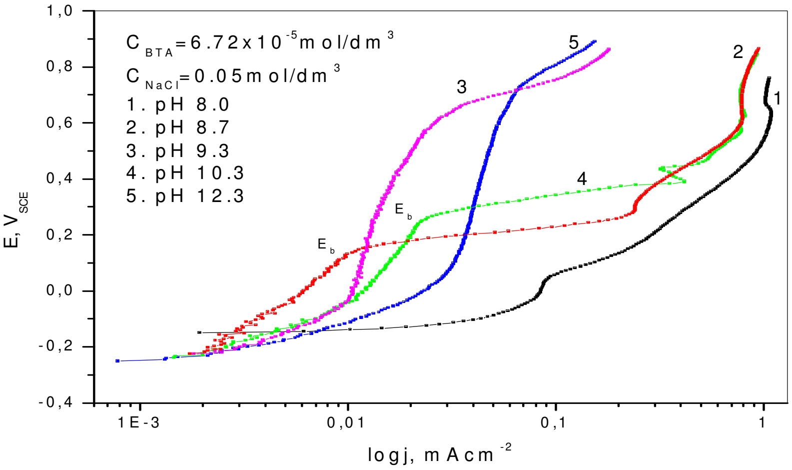

Figure 7. Polarization curves of Cu37Zn in borate buffer solution with addition of $6.72\cdot10^{-5}$M BTA at various pH (8.0; 8.7; 9.3; 10.3; 12.3) with additional of chloride ions (C_{NaCl}=0.05moldm^{-3}). The polarization was done immediately after the electrode immersion in the solutions, 10mVs^{-1}

From Table 7. it is easy to observe that concentration of BTA had a great influence on degree of coverage, and when concentration increase the degree of coverage also increase in the whole observed pH range. With increasing the degree of coverage inhibition efficiency of BTA also increase because the BTA cover larger surface [6]. In chloride containing solution with addition of BTA Mamaş et al. [14] achieved that in a broad range of potential copper can be oxidized to Cu(I) oxides and Cu(II) hydroxides with formation of insoluble Cu(I)BTA film complex. The mechanism of complex film formation is proposed through the reactions [39]:

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

Formation of insoluble, protective, complex film (Cu-BTA) on the electrode surface was elucidated in the earlier paper [25,36,59], and more compact film was discerned in the solution with higher inhibitor concentration [56]. In the chloride solutions the existence of chloride-containing species was detected [17, 38, 60, 61], but in the presence of BTA formation of these species were not observed [36]. Kosec et al. [38, 56] consider that passivation of brass surface in the chloride solution can be caused by formation of Cu(I)-BTA and Zn(II)-BTA polymers, and finally composition of multilayers were: Cu-xZn/Cu_2O,ZnO/Cu(I)-BTA,Zn(II)-BTA. Xue et al. [45] found that the protective film formed onto copper surface was the thinnest in the pH interval from 7.0 to 9.0. Also, solubility of the protective film was the lowest in the same pH interval. Thickness and solubility increase at higher pH and that lead to conclusion that BTA doesn't have good protective property at higher pH, especially at pH 12.0. This is in agreement with results found in present work. Breakdown potential was observed at pH 8.7 and 10.3 at the end of the passive region [39]. An increase of pH shifts the breakdown potential to more positive values. Outside the breakdown potential anodic current density increases which is probably consequence of localized corrosion on the electrode [39].

Table 7. The degree of coverage of brass in borate buffer solutions at various pH, with BTA and NaCl (C_{NaCl}=0.05moldm^{-3}) at potential 0.05V vs. SCE

θ[%]					
C_{BTA}[moldm^{-3}]	pH 8.0	pH 8.7	pH 9.3	pH 10.3	pH 12.3
$3.36\cdot10^{-5}$	-	-	19.45	10.13	23.97
$6.72\cdot10^{-5}$	-	75.08	79.02	37.83	30.81
$6.72\cdot10^{-4}$	94.86	78.74	85.12	63.44	30.08

3.3. Adsorption isotherm

Adsorption of inhibitor on metal surface is the most important step in the mechanism of inhibition [13]. Fig. 8. show the relationship between C/θ and BTA concentration, and results show that BTA was adsorbed on the brass surface according to the Lengmuir's isotherm. The same was observed by other studies [9, 13, 38, 62]. The main equation of Lengmuir's isotherm is:

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

Where θ – is the degree of coverage

ΔG – is adsorption energy

C – is concentration of BTA

K – is the equilibrium constant of the adsorption process

Equation may also be expressed by:

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

The equilibrium constant of the adsorption process can be presented by:

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G}{RT}\right)$$

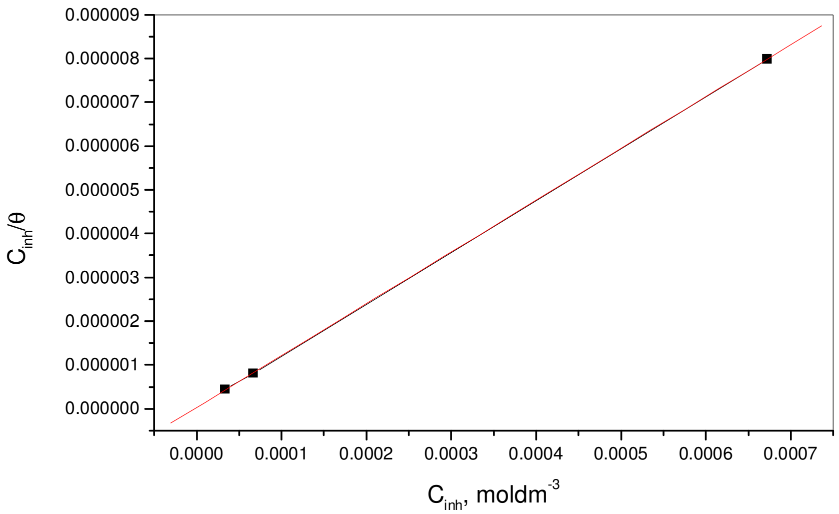

Figure 8. Lengmuir isotherm adsorption model of BTA on the surface of Cu37Zn brass in borate buffer solution at pH=9.3

Table 8. Adsorption energies in borate buffer solution at various pH (8.0, 8.7, 9.3, 10.3, 12.3)

pH	ΔG[kJmol^{-1}]
8.7	-44.94
9.3	-51.86
10.3	-43.30
12.3	-38.66

The negative value of the free energies of adsorption indicates that BTA strongly and spontaneously adsorbed on the brass surface (Tab. 8). Also, the values more negative than -40kJmol^{-1} indicate strong chemisorptions of BTA molecules [9] in the interaction of BTA and electrode surface [58]. Values more negative than -40kJmol^{-1} indicate formation of multilayer protective film on brass surface. Nevertheless, Kosec et al. [38] inferred, on the experimental base, that the inhibition proceeds by chemisorption preferably than by physisorption.

4. CONCLUSIONS

Current density depends on immersion time in 0.2% BTA solution and it is obvious that with increase of immersion time, the current density decrease. Generally current density had the lowest values in the whole potential region when the brass electrode was immersed 60min in 0.2% BTA solution. Moreover increase of pH has influence on current density increase.

In the solution with chloride ions with previous electrode immersion in BTA solution current density increase with increasing potential at all tested pH, and protective film in the vicinity of the corrosion potential is resistant to the effect of chloride ions at all pH.

Open circuit potential becomes more negative when concentration of BTA increases at all pH. However pH also had influence on OCP, make it more negative. In the borax buffer solution with smaller concentration of BTA open circuit potential had more positive values in comparison with solutions which contain Cl^- at the same pH.

Results presented in this paper showed that change of BTA concentration has influence on current density at all observed pH, except at pH 12.3. Generally, current density decreases when BTA concentration increases. Concentration of BTA and pH of solution have an effect on degree of coverage. Degree of coverage increase when BTA concentration and pH increase in the interval from 8.0 to 9.3, but at higher pH (10.3 and 12.3) degree of coverage decrease when pH increases.

Effects of BTA on the anodic current density increase with increasing BTA concentration in the borax buffer solution at pH 9.3 in the presence of chloride ions. Similar results were observed at pH 8.7 but at pH 8.0 only the highest concentration of BTA manifested inhibitive properties. Polarization curves point to that BTA didn't show decrease of current density at pH 12.3, and that was like in the solution without chloride ions. Degree of coverage reveals that BTA has good inhibitive properties in the pH range from 8.0 to 9.3. Also, results lead to inference that in the strongly alkaline solution (pH>10) inhibitive action of BTA decline. Concentration of BTA had a great importance on degree of coverage, and when concentration increase the degree of coverage also increase in the whole observed pH range. With increasing the degree of coverage inhibition efficiency of BTA also increase because the BTA cover higher surface.

BTA was adsorbed on the brass surface according to the Lengmuirs' isotherm. Adsorption is spontaneous and values for ΔG indicating formation of multilayer on brass surface.

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