Corrosion behaviour of \( \text{Cu}_{24}\text{Zn}_5\text{Al} \) alloy in a sodium tetraborate solution in the presence of 1-phenyl-5-mercaptotetrazole

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Received 1 August 2014; accepted 9 December 2014

The electrochemical behaviour of \( \text{Cu}_{24}\text{Zn}_5\text{Al} \) alloy in a sodium tetraborate solution in the presence of 1-phenyl-5-mercaptotetrazole (PMT) has been investigated. Investigations have been carried out on the influence of PMT concentration, chloride ion concentration and the immersion time on the alloy behaviour by employing the technique of mass loss determination and by anodic polarization. Corrosion potential has also been measured and the surfaces of the alloy are recorded using optical microscopy. According to the obtained results 1-phenyl-5-mercaptotetrazole shows good inhibiting properties for the investigated alloy. The inhibition mechanism is based on the formation of a \( \text{Cu-PMT} \) polymer film. Using the Langmuir isotherm the adsorption energy has been found to be in the interval from -33.8 to -37.7 kJ/mol.

**Keywords:** \( \text{Cu}_{24}\text{Zn}_5\text{Al} \) alloy, Corrosion inhibitor, 1-Phenyl-5-mercaptotetrazole

The possibility of corrosion inhibition of copper has been investigated by a great number of researchers. The inhibition of the corrosion process in the presence of some organic compounds containing N and/or S atoms is explained by the fact that through these atoms the bond with transition metals such as copper is readily formed\(^1\)-\(^4\). Inhibition efficiency can be related to the adsorption process, that is, to the formation of a thin film complex on copper surface, which is referred to as the inhibitor-copper bond\(^5\)-\(^8\). Consequently, a great number of copper and copper alloy corrosion inhibitors belong to the group of azoles\(^1\)-\(^3\), amines\(^4\)-\(^8\), amino acids\(^9\)-\(^11\) and others. A copper atom has an unfilled d orbital, which enables the formation of coordinate bonds with the electron donating atoms\(^12\).

The investigations of Ye et al.\(^13\) have shown that a coordination compound formed on copper surface in the presence of 1-phenyl-5-mercaptotetrazole (PMT) inhibits copper corrosion more efficiently than the film formed in the presence of TTA, BTA, MBT, MBI, 2-AP, IBM and in chromates. In the presence of PMT a film forms on copper surface that can be best described as \( \text{Cu-PMT/Cu}_2\text{O/Cu} \) composite structure. By measuring mass loss in a 1 \( \text{mol/dm}^3 \) \( \text{H}_2\text{SO}_4 \) solution in the presence of 1-phenyl-5-mercaptotetrazole and in the absence of the inhibitor, it was established that in the inhibitor solution the mass loss stopped, which is attributed to a strong chemical bond between 5-mercapto 1-phenyl tetrazole and copper surface\(^14\),\(^15\). A molecular structure of PMT is seen in Structure I.

\[ \text{Structure I — Molecular structure of PMT} \]

The nitrogen atom as an electron donor and the –SH group have an important role in the adsorption processes. A PMT molecule is probably absorbed through –S or through a coordinate bond of the –N atom from tetrazole. Szocs et al.\(^16\) investigated the inhibiting properties of PMT in acid sulphate solutions in which PMT proved to be an excellent inhibitor.

The behaviour of copper in sodium tetraborate solutions with and without chloride ions has also been investigated by Milić and Antonijević\(^17\) in the
presence of benzotriazole as the most commonly investigated azole inhibitor. It was found that [Cu(I)BTA] film formed on copper surface. The value of free energy of adsorption pointed to BTA chemisorptions on copper surface. An investigation has also been made into the behaviour of BTA as a corrosion inhibitor of copper alloys (Cu10Zn and Cu45Zn) in chloride solutions and in the presence of BTA, showing a higher degree of inhibition in Cu10Zn alloy. The presence of chloride ions in the solution damages the surface of Cu37Zn alloy; however, in the presence of BTA inhibitor a protective Cu-BTA film forms on the alloy surface preventing the attack of chloride ions.\textsuperscript{19} The subject of this study is the behaviour of copper alloy Cu24Zn5Al in a 0.1 mol/dm\textsuperscript{3} sodium tetraborate solution in the presence and absence of PMT as an inhibitor. Also investigated was the behaviour of this alloy in a 0.1 mol/dm\textsuperscript{3} sodium tetraborate solution in the presence of various concentrations of chloride ions.

**Experimental Section**

**Material**

In order to determine mass loss experimentally the Cu24Zn5Al alloy samples were used. The sample dimensions were 3.0 × 3.0 × 0.5 cm. During electrochemical measurements Cu24Zn5Al alloy was used as the working electrode. It was obtained by immersing Cu24Zn5Al wire, whose surface area was 0.5 cm\textsuperscript{2}, into the methylmethacrilate. Chemical composition of the samples and the electrode was determined by optical emission spectrometer Spectro 20, Germany (Table 1).

**The reagents used in the study**

All the solutions were prepared from the chemicals of p.a. (pro analysis) purity. The solutions for mass loss testing and electrochemical measurements were prepared in the following way:

A 0.1 mol/dm\textsuperscript{3} solution of sodium tetraborate was prepared by dissolving 76.274 g of sodium tetraborate decahydrate in 2 dm\textsuperscript{3} of distilled water.

Solutions of various concentrations of 1-phenyl-5-mercaptopotetrazole (PMT) were prepared in the following way: First, a 1×10\textsuperscript{-2} mol/dm\textsuperscript{3} solution was prepared by dissolving 0.8911 g PMT in a 0.1 mol/dm\textsuperscript{3} sodium tetraborate solution in a vessel whose volume was 500 cm\textsuperscript{3}. From this PMT solution 1×10\textsuperscript{-3}, 1×10\textsuperscript{-4} and 1×10\textsuperscript{-5} mol/dm\textsuperscript{3} solutions were made by dilution. The solutions containing various concentrations of chloride ions were prepared by dissolving 1.4625 g NaCl in 500 cm\textsuperscript{3} of a 0.1 mol/dm\textsuperscript{3} sodium tetraborate solution, which gave a 5 × 10\textsuperscript{-2} mol/dm\textsuperscript{3} chloride ion solution. Other chloride ion solutions (1×10\textsuperscript{-2}, 1×10\textsuperscript{-3} and 1×10\textsuperscript{-4} mol/dm\textsuperscript{3}) were prepared by dilution in a 1 mol/dm\textsuperscript{3} sodium tetraborate solution.

For the investigation of the influence of the time of immersion of the electrode and Cu24Zn5Al alloy samples in the inhibitor solution, a 0.017 mol/dm\textsuperscript{3} PMT solution was used obtained by dissolving 3.0298 g PMT in 1 dm\textsuperscript{3} of a 0.1 mol/dm\textsuperscript{3} sodium tetraborate solution.

**Methods**

**Mass loss measurement**

The samples of the investigated alloy were polished using 1µm grit alumina paste, then rinsed with distilled water, dried, weighed and immersed in the corresponding solutions.

The mass loss of Cu24Zn5Al alloy in a sodium tetraborate solution with the addition of the investigated inhibitor 1-phenyl-5-mercaptopotetrazole (PMT) and chloride ions was investigated in four series.

After each test period (72, 144, 216 and 288 hr) the samples were rinsed, dried and the formed film was removed from the sample surface with hard rubber, whereas the remainder was cleaned with a soft brush, upon which the samples were weighed on analytical scales Pioneer, Ohaus, USA with the precision of measurement 0.0001 g.

All the measurements of the mass loss were performed in triplicate and at room temperature.

**Electrochemical investigations**

Electrochemical measurements were performed on a potentiostat which was directly connected to the computer via an AD card. A classic three-electrode cell was employed with the saturated calomel electrode (SCE) being used as a reference electrode, whereas a platinum electrode was used as an auxiliary electrode. The open circuit potential was measured for five minutes, upon which anodic polarization curves

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Chemical composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>70.91</td>
</tr>
<tr>
<td>Zn</td>
<td>24.00</td>
</tr>
<tr>
<td>Al</td>
<td>5.02</td>
</tr>
<tr>
<td>Fe</td>
<td>0.05</td>
</tr>
<tr>
<td>other</td>
<td>0.02</td>
</tr>
</tbody>
</table>

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Table 1 — Chemical composition of the investigated alloy (%)
were recorded from the open circuit potential up to approximately 1.0V vs. SCE. The measurements were performed at a scan rate of 1 mV/s. Electrochemical properties of the Cu$_{24}$Zn$_5$Al alloy in a sodium-tetraborate solution with the addition of the investigated inhibitor 1-phenyl-5-mercaptotetrazole and chloride ions were examined, too.

**Results and Discussion**

**Mass loss**

**Effect of the inhibitor concentration**

The results obtained during investigation of a spontaneous dissolution of Cu$_{24}$Zn$_5$Al alloy in a 0.1 mol/dm$^3$ sodium tetraborate solution in the presence of various concentrations of the inhibitor 1-phenyl-5-mercaptotetrazole and at various immersion times are shown in Table 2.

Corrosion rate was determined from the mass loss of the alloy by using the following expression:

$$CR = \frac{(m_1 - m_2)}{(A \cdot t)}$$

where $m_1$ represents the mass of the alloy sample prior to the treatment, $m_2$ stands for the mass of the alloy after the treatment, $A$ represents the total surface area of the sample in cm$^2$, $t$-denotes the immersion time in h, and CR represents corrosion rate (mg cm$^{-2}$ h$^{-1}$)

The inhibition efficiency was determined from the corrosion rate data using the following expression:

$$IE\% = \frac{((CR)_0 - (CR)/(CR)_0 ) \cdot 100}{}}$$

<table>
<thead>
<tr>
<th>Solution (mol/dm$^3$)</th>
<th>Immersion time (hr)</th>
<th>Corrosion rate (g cm$^{-2}$ h$^{-1}$)</th>
<th>Inhibition efficiency IE (%)</th>
<th>Degree of coverage ($\theta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>72</td>
<td>8.10·10$^{-7}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>144</td>
<td>5.50·10$^{-7}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>216</td>
<td>4.82·10$^{-7}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>288</td>
<td>4.05·10$^{-7}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>72</td>
<td>6.94·10$^{-7}$</td>
<td>14.3</td>
<td>0.143</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>144</td>
<td>4.63·10$^{-7}$</td>
<td>15.8</td>
<td>0.158</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>216</td>
<td>3.47·10$^{-7}$</td>
<td>57.1</td>
<td>0.571</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>288</td>
<td>2.02·10$^{-7}$</td>
<td>63.2</td>
<td>0.632</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>72</td>
<td>5.79·10$^{-8}$</td>
<td>92.9</td>
<td>0.929</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>144</td>
<td>8.68·10$^{-8}$</td>
<td>84.2</td>
<td>0.842</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>216</td>
<td>5.79·10$^{-8}$</td>
<td>89.5</td>
<td>0.895</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$(0.1)</td>
<td>288</td>
<td>5.79·10$^{-8}$</td>
<td>92.9</td>
<td>0.929</td>
</tr>
</tbody>
</table>
where \((CR)_b\) represents corrosion rate of the investigated alloy in the absence of the inhibitor.

The degree of coverage \((\theta)\) was determined from the expression:

\[
(\theta) = \frac{(CR)_0 - (CR)/(CR)_0}{(CR)_0}
\]

As indicated in Table 2, increased concentrations of 1-phenyl-mercaptotetrazole result in the increased inhibition efficiency. The best protection of the alloy is achieved in solutions with an inhibitor concentration of 0.01 mol/dm³, though at the shortest immersion time (72 hr) the inhibition efficiency was also good even in a 0.001 mol/dm³ inhibitor solution. The inhibiting effect is probably based on the formation of a PMT/copper film. As a result of copper oxidation with the oxygen present in the solution a Cu(I) ion is released which united with 1-phenyl-5-mercaptotetrazole to form a PMT-copper layer. Ye et al. investigated the interaction between copper and 1-phenyl-5-mercaptotetrazole using X-ray photoelectron spectroscopy (XPS) and found that the copper surface contained oxygen, which pointed to copper oxidation. Apart from oxygen, N and S were found, which undoubtedly indicated that a PMT/copper layer formed on copper surface. The results obtained in the mentioned study are in full agreement with the ones presented in this paper.

Scoes et al. investigated the effect of the inhibitor 1-phenyl-5-mercaptotetrazole on copper corrosion in a sulphate solution using the gravimetric method and found that a high inhibition degree was achieved, which is in agreement with the results presented in this paper.

The effect of chloride ion concentration

The effect of chloride ion concentration on corrosion of Cu₃Zn₅Al alloy was investigated by immersing the alloy samples in a sodium tetraborate solution which contained various concentrations of chloride ions \((0.0001 \text{ mol/dm}^3, 0.001 \text{ mol/dm}^3, 0.01 \text{ mol/dm}^3\text{ and } 0.25 \text{ mol/dm}^3 \text{ Cl}^-)\).

After being immersed for 72, 144, 216 and 288 h in the mentioned solutions the samples were taken out, upon which corrosion products were removed and the samples were dried and weighed. The results of those investigations are shown in Table 3. It can be seen from Table 3 in almost all cases that corrosion rate increases with increasing immersion time. As for the effect of chloride ions, it can be said that they do not have a significant influence upon the corrosion rate of the investigated alloy at all immersion times. Furthermore, comparing the corrosion rates of Cu₃Zn₅Al alloy obtained in sodium tetraborate solutions with the one obtained in sodium tetraborate solutions containing chloride ions, it can be concluded that there are no significant differences between them, though in a great number of cases a slightly lower corrosion rate values were obtained in the solutions containing chloride ions.

As corrosion rate is determined for the whole surface of the alloy, corrosion rate values did not differ much for all the investigated concentrations of chloride ions. Moreover, in the presence of chloride ions, the alloy surface may become covered with corrosion products \((\text{CuO, ZnO, Al}_2\text{O}_3)\) which may prevent further oxidation of the alloy.

Using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and energy dispersive X-ray analyser (EDX), Sherif et al. found that Cu, Cl and O were present on copper surface in chloride ion solutions. Since Cu₃Zn₅Al alloy contains 71% copper, it can be assumed that the corrosion products formed on the alloy surface in chloride ion solutions are CuCl and Cu₂O (Ref 24-27).

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Solution concentration</th>
<th>Corrosion rate (g/cm²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na₃B₄O₇ (0.1 mol/dm³)</td>
<td>Na₃B₄O₇ (0.1 mol/dm³)</td>
</tr>
<tr>
<td></td>
<td>Cl⁻ (1·10⁻⁴ mol/dm³)</td>
<td>Cl⁻ (1·10⁻³ mol/dm³)</td>
</tr>
<tr>
<td>72</td>
<td>8.10·10⁻⁷</td>
<td>1.04·10⁻⁶</td>
</tr>
<tr>
<td>144</td>
<td>5.50·10⁻⁷</td>
<td>5.21·10⁻⁷</td>
</tr>
<tr>
<td>216</td>
<td>4.82·10⁻⁷</td>
<td>4.44·10⁻⁷</td>
</tr>
<tr>
<td>288</td>
<td>4.05·10⁻⁷</td>
<td>3.33·10⁻⁷</td>
</tr>
</tbody>
</table>
Copper(I)-oxide can be formed by hydrolysis of CuCl and oxidation of copper:

\[ 2\text{CuCl} + \text{H}_2\text{O} = \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{Cl}^- \]
\[ 2\text{CuCl} + 2\text{OH}^- = \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{Cl}^- \]
\[ 2\text{Cu} + 0.5\text{O}_2 = \text{Cu}_2\text{O} \]

Investigating corrosion behaviour of brass in chloride solutions, Kosec et al.\textsuperscript{18} found that Cu$_2$O was present on brass surface. The presence of corrosion products is most likely the reason why corrosion rate did not change considerably with an increase in chloride ion concentration.

**The effect of pretreatment**

The corrosion behaviour of Cu$_2$Zn$_5$Al alloy which had previously been treated with a 0.017 mol/dm$^3$ solution of 1-phenyl-5-mercaptotetrazole inhibitor was also investigated. The samples were first weighed and then immersed in the inhibitor solution for 1 h, upon which they were rinsed with distilled water and transferred to a sodium tetraborate solution containing chloride ions. The samples were taken from the solution after the corresponding time and then they were dried and weighed after the removal of the corrosion products. The results of those investigations are presented in Table 4.

By comparing the corrosion rates of the alloy presented in Tables 3 and 4, it can be concluded that there are no significant differences between them.

**Electrochemical measurements**

**The effect of 1-phenyl-5-mercaptotetrazole concentration**

Electrochemical behaviour of the alloy Cu$_2$Zn$_5$Al was investigated in a 0.1 mol/dm$^3$ sodium tetraborate solution containing various concentrations of 1-phenyl-5-mercaptotetrazole (1×10$^{-5}$, 1×10$^{-4}$, 1×10$^{-3}$ and 1×10$^{-2}$ mol/dm$^3$). It was found that the open circuit potentials of Cu$_2$Zn$_5$Al alloy for PMT concentrations of 1×10$^{-5}$ mol/dm$^3$, 1×10$^{-4}$ mol/dm$^3$, 1×10$^{-3}$ mol/dm$^3$ and 1×10$^{-2}$ mol/dm$^3$ amounted to -0.186 V, -0.177 V, -0.194 V and -0.242 V, respectively. All the open circuit potential values recorded for Cu$_2$Zn$_5$Al alloy were more negative than the ones recorded when the investigated alloy was immersed in a sodium tetraborate solution without the inhibitor (-0.167 V). This pointed to the reduction properties of 1-phenyl-5-mercaptotetrazole since with the increasing PMT concentration the open circuit potential shifted to the negative region.

The comparison with the open circuit potentials recorded on Pt electrode in the same solutions leads to the same conclusion since all the potential values recorded on Pt electrode in sodium tetraborate solutions containing PMT were more negative than the ones recorded for Pt electrode immersed in the solutions without the inhibitor.

It can be seen from Fig. 1 that all the recorded current density values obtained by polarization of the alloy in the inhibitor solutions (curves 2-5) are lower than the current density values obtained by polarization of Cu$_2$Zn$_5$Al alloy in the inhibitor free solution (curve 1). This indicated that in the vicinity of the corrosion potential, the investigated compound (PMT) has an inhibiting effect. The inhibition mechanism is based on the formation of a Cu-PMT polymer film\textsuperscript{13}. By dissolving more electronegative components, zinc and aluminium, the alloy surface is enriched in copper; thus, the inhibitor can react with Cu$^+$ ions forming a protective film. The peak on polarization curve (curve 1) is attributed to the formation of Cu$_2$O (Ref 28), and it does not occur on polarization curves recorded in the inhibitor solutions.

As indicated by Fig. 1, the lowest current densities are obtained at a PMT concentration of 1×10$^{-3}$ mol/dm$^3$. Mihit et al.\textsuperscript{29} performed polarization

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**Table 4** — Corrosion rate of Cu$_2$Zn$_5$Al alloy in a 0.1 mol/dm$^3$ borax solution and in a 0.1 mol/dm$^3$ borax solution with various Cl$^-$ ion concentrations - pretreatment

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Concentration of the immersion solution</th>
<th>Corrosion rate (g/cm$^2$h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na$_3$B$_4$O$_7$ (0.1 mol/dm$^3$)</td>
<td>Na$_3$B$_4$O$_7$ (0.1 mol/dm$^3$)</td>
</tr>
<tr>
<td></td>
<td>Na$_3$B$_4$O$_7$ (0.1 mol/dm$^3$)</td>
<td>Na$_3$B$_4$O$_7$ (0.1 mol/dm$^3$)</td>
</tr>
<tr>
<td>+Cl$^-$ (1×10$^{-4}$ mol/dm$^3$)</td>
<td>+Cl$^-$ (1×10$^{-3}$ mol/dm$^3$)</td>
<td>+Cl$^-$ (1×10$^{-2}$ mol/dm$^3$)</td>
</tr>
<tr>
<td>72</td>
<td>7.52×10$^{-7}$</td>
<td>4.34×10$^{-7}$</td>
</tr>
<tr>
<td>144</td>
<td>5.11×10$^{-7}$</td>
<td>8.33×10$^{-8}$</td>
</tr>
<tr>
<td>216</td>
<td>3.76×10$^{-7}$</td>
<td>4.24×10$^{-7}$</td>
</tr>
<tr>
<td>288</td>
<td>2.89×10$^{-7}$</td>
<td>4.20×10$^{-7}$</td>
</tr>
</tbody>
</table>
measurements of brass in a 0.2 mol/dm$^3$ HNO$_3$ solution with and without the addition of PMT and came to a conclusion that as the PMT concentration increases the anodic current density decreases and the optimum recorded PMT concentration was 1·10$^{-3}$ mol/dm$^3$.

At the lowest PMT concentration, up to a potential of 0.3 V, current densities are highest compared to the polarization curves recorded in the inhibitor solutions. This is accounted for by the fact that the formation of the protective film proceeds too slowly$^{13}$. It can be seen in Fig. 1, at potentials higher than 0.2 V and at higher inhibitor concentrations (1·10$^{-4}$, 1·10$^{-3}$ and 1·10$^{-2}$ mol/dm$^3$) the current density increases exceeding the values recorded in the inhibitor free solution. Since a protective film forms on the alloy surface preventing its oxidation, this increase in current density can be accounted for by oxidation of PMT inhibitor. Consequently, polarization curves were recorded in the inhibitor solutions of various concentrations but instead of the investigated alloy a platinum electrode was used. The results are shown in Fig. 2.

As indicated by Fig. 2, at low PMT concentrations (1·10$^{-5}$, 1·10$^{-4}$ mol/dm$^3$) (curves 4 and 5) and in the inhibitor free solution (curve 1) current density values differ slightly and are rather low, unlike the current densities observed on curves 2 and 3 which were obtained at higher PMT concentrations (1·10$^{-3}$, 1·10$^{-2}$ mol/dm$^3$). The increased anodic currents can be attributed to the oxidation of 1-phenyl-5-mercaptotetrazole. Nesmerak et al$^{30}$ investigated the composition of the products formed by electrochemical oxidation of 1-phenyl-5-mercaptotetrazole and found using the HPCL method for the identification of products that the main PMT oxidation product was 5-bis-(1-phenyltetrazolyl) disulphide. The reaction of PMT oxidation can be represented by the following equation:

$$\text{2} \text{H}^+ + \text{Ph-N} \overset{\theta}{=} \text{Ph-N-S-S-Ph} + \text{2H}^+$$  \hspace{1cm} \ldots (1)

Since PMT undergoes electrochemical oxidation it can account for an increase in current densities occuring at a potential higher than 0.2 V.

**Adsorption isotherms**

The PMT adsorption mechanism on the alloy surface was examined using the Langmuir isotherm which is obtained from the following relation:

$$\frac{\theta}{1-\theta} = AC \exp\left(-\frac{\Delta G}{RT}\right) = KC$$
where:
K is the constant of the adsorption process
ΔG stands for adsorption free energy
θ denotes degree of coverage
C represents PMT concentration in mol/dm$^3$,
R denotes universal gas constant (8.314 kJ/mol),
T stands for thermodynamic temperature (293 K)
The basic equation is transformed into:
\[
\frac{C}{\theta} = \frac{1}{K} + C
\]

The constant of the adsorption process is determined from the expression:
\[
K = \frac{1}{55.5} \exp \left( \frac{-\Delta G}{RT} \right)
\]

Since corrosion currents could not be determined with certainty from polarization curves, on the basis of which it would be possible to determine the degree of coverage, the degree of coverage (Table 6) was determined at a potential of 0.0 V from the equation:
\[
\theta = \left( j_o - j \right)/j_o,
\]
where $j_o$ represents current density recorded in the inhibitor free solution and $j$ denotes current density recorded in a solution containing PMT.

Figure 3 shows the dependence $C/\theta$ and PMT concentration obtained on the basis of the degree of coverage (Tables 1 and 5).

Adsorption free energy in a sodium tetraborate solution determined on the basis of mass loss, has the values of -34.4, -33.8, -34.1 and -33.9 kJ/mol for immersion time of 3, 6, 9 and 12 days, respectively. This points to a spontaneous adsorption of PMT on copper surface. Adsorption free energy obtained from electrochemical measurements (-37.7 kJ/mol) does not differ much from the data obtained from the mass loss measurements. On the basis of adsorption free energy, it can be said that chemisorption of PMT occurs on the surface of the investigated electrode$^{31}$, which is followed by the formation of a protective polymer film. Yu et al.$^{32}$ investigated the adsorption mechanism and obtained the results indicating that adsorption proceeds in accordance with the Langmuir isotherm and identified the process as chemical adsorption. Mihit et al.$^{31}$ and Subramanian et al.$^{12}$ showed that the adsorption mechanism follows the Langmuir isotherm.

The effect of the immersion time
The effect of the immersion time was examined by immersing Cu$_{24}$Zn$_5$Al electrode in a 0.017 mol/dm$^3$ solution of 1-phenyl-5-mercaptotetrazole for predefined intervals (1, 4 and 48 h), upon which it was rinsed with distilled water and alcohol and transferred to an electrochemical vessel where the open circuit potential was measured and polarization was performed in a 0.1 mol/dm$^3$ sodium tetraborate solution. The results of these investigations are shown in Fig. 4. Based on the recorded open circuit potential values it can be said that when pretreatment was performed in the inhibitor solution the open circuit potential values (-0.149 V, -0.166 V, -0.129 V) were more positive than the values of the open circuit potential established on the investigated alloy which had not been previously treated (-0.167 V). This indicates that during pretreatment a protective polymer film forms on the alloy surface (Cu-PMT) which has a more positive potential than Cu$_{24}$Zn$_5$Al alloy. Figure 4 shows that the lowest current density values were obtained when Cu$_{24}$Zn$_5$Al alloy was immersed in the inhibitor solution for 48 h.
Comparing the results presented in Figs. 1 and 4, it can be concluded that lower current densities are recorded when the investigated alloy is pretreated in the inhibitor solution than when Cu$_{24}$Zn$_5$Al alloy is immersed in a 1-phenyl-5-mercaptotetrazole solution. Our previous investigations show that the same happens when benzotriazole is used as an inhibitor, and considering the fact that the compound 1-phenyl-5-mercaptotetrazole belongs to the azole group, the results presented in this study seem logical.

**The effect of chloride ion concentration**

Electrochemical behaviour of Cu$_{24}$Zn$_5$Al alloy was investigated in a 0.1 mol/dm$^3$ solution containing various concentrations of chloride ions (1×10$^{-4}$, 1×10$^{-3}$, 1×10$^{-2}$ and 5×10$^{-2}$ mol/dm$^3$). The obtained results are presented in Fig. 8. It can be seen in Fig. 5 that all the recorded anodic peak currents occurring on the curves during polarization of Cu$_{24}$Zn$_5$Al alloy in chloride ion solutions are lower than the anodic peak current observed during polarization of the same alloy in sodium tetraborate solutions without Cl$^-$ ions. This points to a mild inhibiting effect of chloride ions, which can be attributed to the formation of protective CuCl and Cu$_2$O layers on the alloy surface.

Similar results were obtained from the measurements of mass loss in chloride solutions which are presented in this study.

As indicated by Fig. 6 showing polarization curves obtained by polarization of Cu$_{24}$Zn$_5$Al alloy which had been previously immersed in a 0.017 mol/dm$^3$ PMT concentration for 1 hour, the investigated inhibitor exhibits good properties in chloride ion solutions and at potentials more negative than 0.3 V there are no peaks which would point to the dissolution of the alloy. All the recorded anodic currents in that potential region are lower than 0.010 mA/cm$^2$. It can also be seen in Fig. 6 that as the concentration of chloride ions
increases at potentials above $E>0.3$ V, anodic currents begin to increase; however, with increasing concentration of chloride ions these currents decrease, which could indicate that at these potentials chloride ions have a mild inhibiting effect. This can be accounted for by the fact that at higher potentials the alloy dissolution takes place, during which copper ions are released. They can react with the Cl$^-$ present on the alloy surface forming insoluble compounds.

**Conclusions**

By measuring mass loss it is found that 1-phenyl-5-mercaptotetrazole has an inhibiting effect. The best protection of the alloy is achieved in solutions with an inhibitor concentration of 0.01 mol/dm$^3$.

By polarization measurements it is found that as the PMT concentration increases anodic current density decreases in the vicinity of the corrosion potential, which indicates that PMT behave as corrosion inhibitor of Cu$_{24}$Zn$_5$Al alloy.

Based on the value of adsorption free energy it can be said that PMT chemisorption takes place on the surface of the investigated alloy which is followed by the formation of a protective layer. It is found that the adsorption of the inhibitor occurs in accordance with the Langmuir isotherm. The adsorption energy value for PMT in a sodium tetraborate solution ranges from -33.8 to -37.7 kJ/mol, indicating that PMT is spontaneously adsorbed on copper surface.

The investigation which included a pretreatment of the alloy surface in a 0.017 mol/dm$^3$ inhibitor solution points to the formation of a protective layer (Cu-PMT).

Chloride ions did not have a considerable effect on the corrosion of Cu$_{24}$Zn$_5$Al alloy in the investigated solutions.

**Acknowledgements**

The authors gratefully acknowledge the financial support of the Ministry of Science of Serbia through the Project No 172031

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