Corrosion Inhibition and Dezincification of Brass in % 3 NaCl Solution by 3-Phenyl-1,2,4-Triazol-5-Thione

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Abstract- The dezincification of brass is a problem that has often been encountered in the process of corrosion of brass in aqueous solution. Thus the inhibiting substances must be used to reduce the dissolution of these metallic materials. The present work aimed to study the effect of 3-phenyl-1,2,4-triazole-5-thione (PTS) on Cu/Zn brass corrosion in 3% NaCl solution. This latter is prepared with a new method in our laboratory. The efficiency of (PTS) as brass (alloy 60 Cu-Zn) corrosion inhibitor in %3 NaCl solution was investigated using electrochemical impedance spectroscopy and potentiodynamic measurements. The results showed that the PTS is an excellent inhibitor. The inhibiting efficiency increased by an increase of its concentration. At $10^{-3}$ M the important polarization resistance value of the anodic branch at high current density is believed to be due to the resistance of the inhibitor film formed. The spectroscopic techniques showed that the PTS can be also used as an inhibitor of the dezincification of the brass in the same solution. Consequently, we have concluded that the PTS has good inhibiting effect to stop brass dezincification phenomenon.

Key words– Dezincification, 3-phenyl-1,2,4-Triazole-5-Thione, Inhibition, Brass, %3 NaCl

1. INTRODUCTION

The alloys of Cu-Zn are known as brass. These alloys contain the best mechanic properties [1]. Numerous studies have shown that triazole derivatives have useful corrosion effects [2-4]. The most efficient compound is heterocyclic derivatives containing N and S,
due to their action as multiple active centers for chemisorption. Studies on the corrosion inhibition of brass with organic additives are reported in references [5-7]. The present work aimed to study the effect of PTS on brass corrosion in %3 NaCl solution. The PTS has been synthesized using a new method [8]. Its structure is shown in figure 1. Following the previous works carried out in our laboratory concerning the use of some heterocyclic compounds as corrosion inhibitors [9-11], in this work, we study in one hand the effect of addition of PTS on the corrosion resistance of brass in %3 NaCl. At this purpose the action of PTS on the anodic and cathodic behavior was evaluated by potentiodynamic polarization tests and electrochemical impedance measurements (EIS). On the other hand, we have shown that PTS protects the brass against dezincification at $10^{-3}$ M for a long immersion time in %3 NaCl solution. These studies have focus attention on the nature of protective films formed on the alloys surface, and the problems of selective dissolution of zinc. This latter could present a serious economic problem to both the water industry and its customers.

2. EXPERIMENTAL

2.1. Inhibitor

The 3-phenyl-1,2,4-triazol-5-thione (PTS) was prepared from the action of thiosemicartbazid on the methylbenzoate [8], the resulting product recristalised from water and characterized by IR and NMR spectroscopy.

![Molecular structure of PTC synthesised](image)

Fig.1. Molecular structure of PTC synthesised

2.2. Spectral characteristics

IR (KBr, cm$^{-1}$): 1628 ($\nu_{C=\text{N}}$), 1070($\nu_{\text{C=S}}$), 3066($\nu_{\text{N-H}}$).

$^1$H NMR (60 MHz, DMSO d6) δ: 14.50 (s, 2H), 8.67-7.50 (m, 5H).
$^{13}$C NMR (75 MHz, DMSO d6) $\delta$: 181.92, 165.77, 132.36, 131.69, 128.10, 127.76

2.3. Electrolyte solution

The electrolyte solution was 3% NaCl, which was prepared by diluting in distilled water, reagent grad NaCl “prolabo mark”. All tests have been carried out, unless otherwise, in aerated solution at 25°C.

2.4. Brass samples

The sample was commercial brass of the following chemical composition: Cu 60.61; Zn 39.19; Al 0.12; Si 0.08. The Samples were cut in circular with 1.92 cm$^2$ of side surface.

2.5. Electrochemical techniques

2.5.1. Polarization measurements

Electrochemical measurements were conducted in a cell with conventional three-electrode. A platinum disc was used as counter electrode and the Ag-AgCl as reference electrode. The working electrode was brass disc. The specimens were machined into cylinders and mounted in polytetra-fluoroethylene (PTFE) moulds. The area in contact with the corrosive solution was 1.92 cm$^2$. Before each experiment, the specimens were polished mechanically successively with 600, 1000 and 1200 grade emery papers. Then degreased in acetone and finally dried with hot air.

The potentiodynamic polarization curves were recorded using an EG&G 352 A instrument. The working electrode was initially immersed for 1h in the tests solution in free corrosion conditions. Then the cathodic an anodic curves were recorded by changing stepwise (30 mv/ mn) the potential and the rate of rotating electrode is 1000 tr/mn.

2.6. Electrochemical Impedance Spectroscopy measurements

Electrochemical Impedance spectroscopy (EIS) measurements were done by using Solartron Schlumberger 1250 apparatus. Normally the investigated frequency interval ranged from 65 KHz to 1 mHz. 5 mV (rms) sinusoidal potential perturbations were applied in these tests which were performed in the potentiostatic mode at the corrosion potential at 1hour of immersion time.

2.7. Surface analysis

The analytical methods used as the following:
- Electron spectroscopy for chemical analyses (ESCA)
- Scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX).

The determinations of atomic concentrations of Cu and Zn have been mad with PHI (V006) programme.
3. RESULT AND DISCUSSION

3.1. Potentiodynamic measurements

Cathodic and anodic polarization curves in aerated 3% NaCl solution without and with addition of inhibitor (PTS) at different concentrations are shown in Fig. 2.

![Cathodic and anodic current-voltage curves](image)

**Fig. 2.** Cathodic and anodic current-voltage curves of brass in aerated 3% NaCl solution at various PTS concentrations at 25 °C

We note that the additions of PTS leads to a decrease in cathodic and anodic current densities with a slight shift of corrosion potential toward positive values are observed when the concentration of inhibitor increases.

In the cathodic curves, it should be shown that an increase of PTS concentration (from $10^{-4}$ to $10^{-3}$ M) clearly reduces the cathodic current on a more extended potential range. The lowest cathodic currents were obtained at $10^{-3}$ M of PTS. At sufficient negative potentials in this range, the cathodic current reaches a plateau (il), owing to diffusion limitations in the cathodic reduction reaction. This cathodic current plateau noted in presence of inhibitor and which value reaches that obtained in blank essay may be explained by a desorption of the PTS inhibitor.

In the anodic branch, in the presence of PTS, the current density values are significantly lowered on a large potential range. The above effect is more marked as the inhibitor concentration increases. At $10^{-3}$ M of PTS, the brass becomes passive at $i=0.3 \mu A/cm^2$ with over potential $\theta_{Ag-AgCl}$ showed the formation of the protective layer of inhibitor.

Examination of this curve shows that the values of anodic current densities increase sharply when the potential becomes more anodic especially when its value becomes higher.
than 0.2 V/Eag, AgCl to join the curve of the witness. This behavior implies that the inhibitor film is destroyed at high anodic overvoltage.

Values of associated electrochemical parameters such as corrosion potential ($E_{corr}$), cathodic tafel slope ($bc$), corrosion current density ($I_{corr}$) and inhibitor efficiencies (%$E$) for the PTS compound are given in Table 1.

**Table 1.** Electrochemical parameters from polarization measurements on brass in %3 NaCl without ant with different inhibitor concentrations

<table>
<thead>
<tr>
<th>PTS (M)</th>
<th>$E_{corr}$ V(Ag-AgCl)</th>
<th>$I_{corr}$ (µA/cm²)</th>
<th>$bc$(mv/dec)</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.264</td>
<td>77.01</td>
<td>258</td>
<td>93.4</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>-0.226</td>
<td>5.01</td>
<td>195</td>
<td>98.7</td>
</tr>
<tr>
<td>$510^{-4}$</td>
<td>-0.197</td>
<td>0.96</td>
<td>145</td>
<td>99.7</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>-0.156</td>
<td>0.22</td>
<td>148</td>
<td>99.7</td>
</tr>
</tbody>
</table>

The results depicted in table1 show a decrease of the corrosion current density with increasing of PTS concentrations. Indeed it was shown that PTS give a maximum inhibiting effect at $10^{-3}$ M (%99.7). So we're limited at this inhibitor concentration

**3.2. Electrochemical Impedance spectroscopy measurements**

The aim of this study is to obtain more information concerning the electrochemical process which carried at the brass / %3 NaCl interface in presence of $10^{-3}$ M of PTS. The Nyquist plots obtained with and without inhibitor are given in Fig. 3.

In the absence of the inhibitor, the impedance diagram (Nyquist plot) of brass is characterized by two poorly resolved capacitive loops. In agreement with that found on pure copper [12-14], the impedance spectra obtained at $E_{corr}$ can be ascribed to a corrosion process depending on mass transfer through a porous layer of corrosion products.

In the presence of PTS the impedance diagrams are characterized by two time constants. The high frequency section is distorted. In the low frequency range the diagrams do not close on the real axis. In the high frequency region of the diagram a linear part is evident, with a slope close to 1. Such a behavior is generally ascribed to Warburg diffusion effects in solid phase. The $R_p$ value passes from 0.6 K Ohm cm² without inhibitor to 50 K Ohm cm² with inhibitor, so that the inhibition efficiency defined as: [$%E=(1- R_p/R_{p0}) *100$. Where $R_p$ and $R_{p0}$ are the polarization resistance with and without inhibitor respectively] is around %98. This value is in good agreement with the previous electrochemical results. The calculated
capacity value from the relation $C=(2\pi f R)^{-1}$ (where $f$ is maximum frequency of the loop and $R$ is the diameter of capacitive loop) is approximately around 46.7 µF without inhibitor and 1.79 µF in presence of 1 mM of PTS.

Fig. 3. Electrochemical impedance spectra of brass in %3 NaCl without (a) and with PTS (b) obtained at free corrosion potential for 1 h of immersion times, 1000 rpm
This low capacity value makes it justifiable to ascribe the loop to a thick inhibitor layer formation on the electrode surface. The impedance diagram part in low frequencies range represents the faradic processes occurring on the electrode surface where the proposed inhibitor film fails.

3.3. Gravimetric measurements.

The dezincification of brass is a problem that has been met in process of brass corrosion in aqueous solution. Several works have been performed in order to find a solution to the problem of brass dezincification [15-17]. In this study, we have followed the evolution of Cu-Zn ratio towards immersion time and anodic polarization. We have used atomic absorption technique for the determination of the Cu and Zn ions dissolved, and the ESCA spectra.

3.4. Study at the corrosion potential

Table 2, compare the theoretical value of the Cu/Zn ratio for the brass with data calculated from the determination of ions dissolved in the function of immersion time without and with 1 mM of PTS.

3.5. Evolution of the Cu/Zn ratio in function of the anodic polarization:

In this study, we have examined the anodic potential effect towards the corrosion products composition after an immersion time of one hour. Table 3 reported the values of the Cu/Zn ratio at different anodic potentials.

Table 2. Values of Cu / Zn ratio for 60 Cu-Zn brass without and with PTS at different immersion times.

<table>
<thead>
<tr>
<th>Times (hours)</th>
<th>Cu /Zn ratio (without PTS)</th>
<th>Cu /Zn ratio (with PTS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.45</td>
<td>1.54</td>
</tr>
<tr>
<td>2</td>
<td>0.63</td>
<td>1.52</td>
</tr>
<tr>
<td>3</td>
<td>0.72</td>
<td>1.50</td>
</tr>
<tr>
<td>4</td>
<td>0.88</td>
<td>1.51</td>
</tr>
<tr>
<td>5</td>
<td>1.08</td>
<td>1.51</td>
</tr>
<tr>
<td>6</td>
<td>1.24</td>
<td>1.50</td>
</tr>
<tr>
<td>24</td>
<td>1.24</td>
<td>1.49</td>
</tr>
<tr>
<td>48</td>
<td>1.51</td>
<td>1.51</td>
</tr>
<tr>
<td>72</td>
<td>-</td>
<td>1.48</td>
</tr>
<tr>
<td>120</td>
<td>-</td>
<td>1.48</td>
</tr>
</tbody>
</table>
This table shows that:

- In 3% NaCl solution, the Cu/Zn ratio are very weak for the immersion time inferior of 5 h. A selective dissolution of zinc is initially evident.
- For the long immersion times, the Cu/Zn increases considerably to attain a value very similar to the corresponding theoretical value after 24 h, so both Cu and Zn are dissolved.
- In the presence of 1 mM of PTS, the Cu / Zn ration is maintained at a value very close to the theoretical value (1.5). This result shows that PTS is an inhibitor of dissolution of both Cu and Zn.

**Table 3.** Values of Cu/Zn ratio of 60 Cu-Zn alloy in function of the anodic potential in 3% NaCl

<table>
<thead>
<tr>
<th>Imposed potential (V/Ag-AgCl)</th>
<th>Cu/Zn ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.206</td>
<td>1.49</td>
</tr>
<tr>
<td>-0.100</td>
<td>1.23</td>
</tr>
<tr>
<td>-0.100</td>
<td>1.12</td>
</tr>
<tr>
<td>-0.350</td>
<td>0.85</td>
</tr>
<tr>
<td>-0.500</td>
<td>0.19</td>
</tr>
<tr>
<td>-0.600</td>
<td>0.65</td>
</tr>
<tr>
<td>-0.700</td>
<td>1.23</td>
</tr>
<tr>
<td>-0.800</td>
<td>1.49</td>
</tr>
</tbody>
</table>

The result obtained in Table 3, shows that for the value of potential between $E_{corr}$ and 0.5 V/Ag-AgCl, the Cu/Zn decreases, which may indicate an effective dissolution of Zn constituent of brass. more important of copper one. For this later this less dissolution may be attributed to copper oxide and chloride formation which may react with zinc. In accordance of a detailed study discussed elsewhere [18], the increase and saturated CuCl$_2$ concentration on the alloy surface leads to the precipitation of CuCl. The presence of these tow compounds in solution leads to the redeposit the copper as:

\[
2\text{CuCl} + Zn \leftrightarrow 2\text{Cu} + \text{ZnCl}_2
\]

\[
\text{CuCl}_2 + Zn \leftrightarrow \text{Cu} + \text{ZnCl}_2
\]

At potential higher than 0.5 V, the value of analysed ratio increases to reach the theoretical value. Can be explained by formation of corrosion products which cover all sample surface and decrease the dezincification phenomenon. This in agreement with anodic polariuzation curve which shows a pleau of anodic current.
Fig. 4 shows the ESCA spectra of 60 Cu-Zn sample after polarization at respectively 0.1 and 0.5 V\textsubscript{Ag-AgCl} in 3% NaCl during one hour.

This figure shows the following results:
- After polarization at $E=0.1$ V\textsubscript{Ag-AgCl}:
  
  The spectrum reveals the presence of two peaks: one at 917 eV, which can be assigned to the presence of Cu\textsubscript{2}O, and another small at 919 eV can be attributed to a few quantity of
copper as metal on the alloy surface. Concerning the Zinc, the presence of one peak at 992 eV is characteristic of the transformation the Zn to ZnO.

• After polarization at E = 0.5 V Ag-AgCl:
  
The copper is as Cu° form with a weak quantity of Cu₂O. This later confirms the presence of copper film on the alloy surface.

• The presence of the CuCl and CuCl₂ on the alloy surface

• Concerning the Zinc, we observe the presence of the ZnO and ZnCl₂ products.

For the anodic potential superior at +0.6 V Ag-AgCl, the Cu/Zn ratio increases to attain a value approximate to the theoretical value of the alloy (1.54). This can be interpreted by the fact that at this potential, there is no formation of CuCl₂. Therefore the process of deposition of copper stopped.

3.6. Characterization of the PTS film formed on the 60 Cu-Zn alloys surface using EDS

The aim of this study is to check the hypothesis of the formation of the inhibitor film on the alloy surface, and try to see under which form the PTS exists on the alloy surface.

In Fig. 5 we have reported the EDS analyses realized for brass specimens after immersion during 4 h at Ecorr without and with 10⁻³ M of PTS. In the presence of 10⁻³ M of PTS, The EDS exam confirms the presence of the organic substance on the surface of the studied alloy. We note the presence of picks corresponding to C, N and S atoms.

The value of the Cu/Zn ratio is sensibly equal to 0.1. Also the presence of O is emphasized. This can be correlated with the ability of copper to react with oxygen. These results suggest the formation of an inhibitor film on the brass electrode, and the formation of chemisorbed monolayer Cu₂O film, and its growth involved precipitation of Cu and Zn ions may be as highly insoluble Cu-Zn-PTS complexes at the solid / liquid interface.

![Fig. 5. EDS spectra obtained on the 60 Cu-Zn surface: a) After immersion during 4 h at Ecorr in pure 3NaCl b) After immersion during 4 h at Ecorr in 3 NaCl + 10⁻³ M of PTS](image-url)
The obtained results using analytical techniques confirm the results obtained using electrochemical measurements (polarization curves and impedance measurements). So we confirm that the PTS is an excellent inhibitor of brass in 3% NaCl acting by formation of film on the electrode surface.

4. CONCLUSION

The effect of PTS inhibitor on the corrosion of brass in sodium chloride medium solution was examined in this paper. For this sake, the cathodic and anodic processes of brass electrode in %3 NaCl solution in presence of various PTS concentrations were analyzed. The results obtained show that the PTS acts by restraining both the cathodic and anodic reactions; this protective action was due to the inhibitor films acting as efficient physical barriers. This later is confirmed by EIS spectra.

The gravimetric study show that, in the presence of PTS the Cu /Zn ratio is maintained for the long immersion times at a value very close to the theoretical one indicating the good inhibiting effect to protect copper and zinc elements.

The EDX analysis shows that the protection of brass is due to the formation of chemisorbed film and the Cu, Zn ions then react with physically absorbed PTS molecules to precipitate insoluble Cu-Zn-PTS complexes at the solid / liquid interface.

REFERENCES