Effect of 4-phenyl4-phenylthiazole derivatives on preventing dezincification of α-brass in acid chloride solution

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Abstract
The influence of some 4-phenyl4-phenylthiazole derivatives on preventing dezincification of α-brass in acid chloride solution has been studied using galvanostatic polarization technique. In general at constant acid concentration, inhibition efficiency increases with increasing concentration of inhibitors and decreases with rise in temperature. Polarization studies revealed that these compounds behave as cathodic inhibitors. The effect of temperature on corrosion of the alloy has been studied and the activation energies and some thermodynamic parameters are calculated and discussed. The adsorption of the inhibitors on α-brass surface is found to obey Timken's adsorption isotherm. Addition of I− ions to the acidic medium containing some 4-phenyl4-phenylthiazole derivatives increase the inhibition efficiency of the system.

Keywords: Brass, dezincification, HCl, 4-phenyl4-phenylthiazole derivatives

1. Introduction
Brass alloys are characterized by their excellent thermal conductivity and mechanical workability [1]. They are widely used as tubing material in condensers and as heat exchangers for water cooling systems [2]. In spite of its important industrial applications, brass suffers from corrosion in aqueous environments containing corrosive ions such as chloride and sulfate. Corrosion manifests itself dezincification when active component zinc tends to dissolve selectively out of the alloy, leaving its surface enriched in copper [3, 4]. Dezincification causes undesirable changes in the surface and mechanical properties of the alloy. It caused the the premature failure in heat exchanger tubes in power stations in Spain and in Turkey [5, 6]. Dezincification has been widely investigated [7-14] especially in salt water [3, 8 & 9]. Many inhibitors have been used to minimize the corrosion of brass in different media [15]. There are many applications in corrosion inhibition of copper alloys using heterocyclic organic compounds containing nitrogen, sulphur and/or oxygen atoms, e.g. amino-pyrazole [16, 17], amino-thiazole and triazole thiols [18, 19]. Very little literature [20, 21] investigated the effect of oxidizing agents on the corrosion of brass under free corrosion conditions.

This paper aims to study the protection efficiency of some 4-phenyl4-phenylthiazole derivatives towards the corrosion of α-brass in acid solution, and to predict the thermodynamic ability of the inhibitors to adsorb on the α-brass surface and to throw some light on the mechanism of inhibition of these derivatives.

2. Experimental
2.1. Materials
The experiments were performed on α-brass having the chemical composition: 72% Cu, 27.94% Zn, 0.02% Fe, 0.02% Ni and 0.02% Pb.
The brass specimens were polished mechanically with silicon carbide papers from 120 to 1200 grit followed by 5µm diamond paste. The electrodes were thoroughly washed with double distilled water and degreased in acetone for 2 min using ultrasonic vibration and dried [22]. The solutions were prepared from analar grade chemicals using double distilled water. A series of 4-phenyl4-phenylthiazole derivatives were used as organic inhibitors. The 4-phenyl4-phenylthiazole derivatives were prepared as described earlier by Metwally et al [23] and their structures are given below:

(a) 2-amino-5-(p-methoxyazobenzene)-4-phenyl-thiazole

(b) 2-amino-5-(p-methylazobenzene)-4-phenyl-thiazole

(c) 2-amino-5-azobenzene-4-phenyl-thiazole

(d) 2-amino-5-(p-bromoazobenzene)-4-phenyl-thiazole

(e) 2-amino-5-(p-nitroazobenzene)-4-phenyl-thiazole

2.2. Electrochemical measurements

Galvanostatic polarization studies were carried out on α-brass in 0.5 M HCl solution with and without different concentrations of the investigated inhibitors at 30 °C. A cylindrical rod with a surface area of 1 cm² and a diameter of 1.25 mm was used as working electrode. Saturated calomel electrode (SCE) was used as reference electrode while a platinum wire as a counter electrode. All experiments were carried out at 30 ± 1°C. The inhibition efficiency (% IE) is defined as:

\[
\text{% IE} = \left(\frac{j_{\text{corr}} - j_{\text{inh}}}{j_{\text{corr}}}\right) \times 100
\]

where \(j_{\text{corr}}\) and \(j_{\text{inh}}\) are the uninhibited and inhibited corrosion current densities, respectively.
3. Results and discussion

3.1. Polarization measurements

Fig. 1 shows the galvanostatic polarization curves (E vs log j) of α-brass dissolution in 0.5 M HCl, in presence of different concentrations of compound (a) at 30 °C. Similar curves were obtained for other derivatives (not shown). An increase in the concentration of inhibitors shift the polarization curves towards more negative potentials relative to the blank curve for cathodic polarization, but in case of anodic polarization, the curves in presence of inhibitors lie on that of the free acid. This indicates that these inhibitors affect only the cathodic polarization and act as cathodic inhibitors. The corrosion potential (E_{corr}), cathodic Tafel slope (β_c), degree of surface coverage (θ) and percentage inhibition (% IE) were derived from the curves of Fig. 1, are recorded in Table 1. As shown from this Table the corrosion current density (j_{corr}) decreases with increasing the concentration of 4-phenylthiazole derivatives, which indicates that the presence of these derivatives retards the dissolution of α-brass in 0.5 M HCl solution and the degree of inhibition efficiency depends on the concentration and type of the inhibitor present. The inhibition efficiency is decreased in the following order: a > b > c > d > e.

![Galvanostatic polarization curves](image)

**Fig. 1** Galvanostatic polarization curves for α-brass corrosion in 0.5 M HCl in absence and presence of different concentrations of compound (a) at 30 °C

<table>
<thead>
<tr>
<th>Conc., M</th>
<th>j_{corr}, µA cm^{-2}</th>
<th>E_{corr}, mV</th>
<th>β_c, mV dec^{-1}</th>
<th>θ</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>55</td>
<td>252</td>
<td>810</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1x10^{-6}</td>
<td>38</td>
<td>265</td>
<td>571</td>
<td>0.230</td>
<td>23.0</td>
</tr>
<tr>
<td>3x10^{-6}</td>
<td>30</td>
<td>285</td>
<td>488</td>
<td>0.390</td>
<td>39.0</td>
</tr>
<tr>
<td>5x10^{-6}</td>
<td>23</td>
<td>294</td>
<td>415</td>
<td>0.520</td>
<td>52.0</td>
</tr>
<tr>
<td>7x10^{-6}</td>
<td>19</td>
<td>291</td>
<td>437</td>
<td>0.600</td>
<td>60.0</td>
</tr>
<tr>
<td>9x10^{-6}</td>
<td>15</td>
<td>301</td>
<td>249</td>
<td>0.670</td>
<td>67.0</td>
</tr>
<tr>
<td>11x10^{-6}</td>
<td>11</td>
<td>304</td>
<td>263</td>
<td>0.710</td>
<td>71.0</td>
</tr>
</tbody>
</table>
3.2. Synergistic Effect

The effect of addition of $1 \times 10^{-2}$ M KI to different concentrations of inhibitor (a) on the corrosion inhibition of $\alpha$-brass in 0.5 M HCl using galvanostatic polarization was studied (Fig. 2). From the calculated values of % IE given in Table 2, it is observed that % IE of the inhibitors increases on addition of KI salt due to synergistic effect of the anion in combination with cation of the inhibitor. The cation is then adsorbed by cumbic attraction on the metal surface where these ions are already adsorbed by chemisorption. Stabilization of this adsorbed anion with cations leads to greater surface coverage and therefore greater inhibition.

The synergistic inhibition effect was evaluated using a parameter, $S_0$, obtained from the surface coverage values ($\theta$) of the anion, cation and both. Aramaki and Hackerman [24] calculated the synergism parameter $S_0$ using the following equation:

$$S_0 = \frac{(1 - \theta_{1+2})}{(1 - \theta'_{1+2})}$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, $\theta_1$ is the surface coverage by anion, $\theta_2$ is the surface coverage by cation and $\theta'_{1+2}$ is the measured surface coverage for cation in combination with halides. This equation actually compares the corrosion rate of either anion or cation and of inhibitor mixture (cation + anion). If anions and cations have no effect on each other and adsorbed at metal surface independently, the $S_0$ value should be 1. Furthermore, synergistic effects are observed if $S_0 > 1$ and activation of corrosion is observed if $S_0 < 1$.

The synergism parameters ($S_0$) were calculated from the above equation and are presented in Table 3. As can seen from Table 3, the values of synergism parameters of investigated compounds are greater than unity, which suggests that the enhanced inhibition efficiency was caused by the addition of KI to 4-phenyl4-phenylthiazole derivatives mainly due to the synergistic effect.

![Galvanostatic polarization curves](image-url)

Fig. 2 Galvanostatic polarization curves for $\alpha$-brass dissolution in 0.5 M HCl in the absence and presence of different concentrations of compound (a) with addition of $1 \times 10^{-2}$ M KI at 30°C
Table 2 % Inhibition efficiency of $\alpha$-brass dissolution in 0.5 M HCl in presence of different concentrations of 4-phenyl4-phenylthiazole derivatives with addition of $1x10^{-2}$ M KI at 30 °C

<table>
<thead>
<tr>
<th>Conc., M</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1x10^{-6}$</td>
<td>53.0</td>
<td>49.7</td>
<td>46.1</td>
<td>43.5</td>
<td>40.0</td>
</tr>
<tr>
<td>$3x10^{-6}$</td>
<td>64.4</td>
<td>61.8</td>
<td>59.1</td>
<td>56.2</td>
<td>53.0</td>
</tr>
<tr>
<td>$5x10^{-6}$</td>
<td>67.5</td>
<td>67.5</td>
<td>65.2</td>
<td>62.7</td>
<td>59.1</td>
</tr>
<tr>
<td>$7x10^{-6}$</td>
<td>77.0</td>
<td>71.0</td>
<td>69.0</td>
<td>66.7</td>
<td>65.2</td>
</tr>
<tr>
<td>$9x10^{-6}$</td>
<td>79.5</td>
<td>74.8</td>
<td>73.0</td>
<td>70.4</td>
<td>68.2</td>
</tr>
<tr>
<td>$11x10^{-6}$</td>
<td>87.1</td>
<td>83.7</td>
<td>81.7</td>
<td>77.5</td>
<td>74.4</td>
</tr>
</tbody>
</table>

Table 3 Synergism parameter ($S_0$) for different concentrations of 4-phenyl4-phenylthiazole derivatives for $\alpha$-brass dissolution in 0.5 M HCl with addition of $1x10^{-2}$ M KI at 30 °C

<table>
<thead>
<tr>
<th>Concentration, M</th>
<th>Synergism parameter ($S_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>$1x10^{-6}$</td>
<td>1.11</td>
</tr>
<tr>
<td>$3x10^{-6}$</td>
<td>1.14</td>
</tr>
<tr>
<td>$5x10^{-6}$</td>
<td>1.11</td>
</tr>
<tr>
<td>$7x10^{-6}$</td>
<td>1.17</td>
</tr>
<tr>
<td>$9x10^{-6}$</td>
<td>1.05</td>
</tr>
<tr>
<td>$11x10^{-6}$</td>
<td>1.34</td>
</tr>
</tbody>
</table>

3.3. Effect of temperature and activation parameters

The effect of temperature on the corrosion rate of $\alpha$-brass in 0.5 M HCl solution in the absence and presence of $9x10^{-6}$ M of 4-phenyl4-phenylthiazole derivatives was studied in the temperatures range of (30-50 °C) using galvanostatic polarization measurements. Similar curves for other 4-phenyl4-phenylthiazole derivatives were obtained (not shown). As the temperature increases, the rate of corrosion increases and hence the inhibition efficiency of the additives decreases. This is due to the desorption of the adsorbed molecules of the inhibitors from the metal surface. This behavior proves that the adsorption of inhibitors on $\alpha$-brass surface occurs through physical adsorption.

The apparent activation energies $E_a^\ast$, the change in enthalpies of activation $\Delta H_a^\ast$ and the change in entropies of activation $\Delta S_a^\ast$ for the corrosion of $\alpha$-brass sample in 0.5 M HCl solution in the absence and presence of different concentrations of 4-phenyl4-phenylthiazole derivatives at 30, 35, 40, 45 and 50 °C were calculated from Arrhenius-type [25] equation:

$$\text{Rate} = A \exp \left( \frac{-E_a^\ast}{RT} \right) \quad (3)$$

and transition-state equation:

$$\text{Rate} = \frac{RT}{Nh} \exp \left( \frac{\Delta S^\ast}{R} \right) \exp \left( \frac{-\Delta H^\ast}{RT} \right) \quad (4)$$
where $A$ is the frequency factor, $h$ is the Planck’s constant, $N$ is Avogadro’s number and $R$ is the universal gas constant. A plot of log Rate vs. $1/T$ and log (Rate/T) vs. $1/T$ give straight lines with slopes of $-E_a^*/2.303R$ and $-\Delta H^*/2.303R$, respectively. The intercepts will be $A$ and log $R/Nh + \Delta S^*/2.303R$ for Arrhenius and transition state equations, respectively.

Fig. (3) represents plots of the log corrosion rate vs. $1/T$ and Fig. (4) represents plots of log (rate/T) vs. $1/T$. The calculated values of the apparent activation energy, $E_a^*$, activation entropies, $\Delta S^*$, and activation enthalpies, $\Delta H^*$, are given in Table 4.

The almost similar values of $E_a^*$ suggest that the inhibitors are similar in the mechanism of action and the order of efficiency may be related to the preexponential factor $A$ in equation (3). This is further related to concentration, steric effects and metal surface characters. The positive values of $\Delta H^*$ reflect that the process of desorption of the inhibitors on the brass surface is endothermic process. The values of $\Delta S^*$ in the presence and absence of the inhibitors is large and negative. This implies that the activation complex is the rate determining step represents association rather than dissociation, indicating that a decrease in disorder takes place on going from reactants to the activated complex [26].

Fig. 3 Log corrosion rate vs. $1/T$ curves for $\alpha$-brass dissolution in 0.5 M HCl in the absence and presence of $9 \times 10^{-6}$ M different 4-phenylthiazole derivatives

Fig. 4 log (corrosion rate / T) vs. $1/T$ curves for $\alpha$-brass dissolution in 0.5 M HCl in absence and presence of $9 \times 10^{-6}$ M different 4-phenylthiazole derivatives
3.4. Adsorption isotherm

The values of the degree of surface coverage $\theta$ were evaluated at different concentrations of the inhibitors in 0.5 M HCl solution. Attempts were made to fit $\theta$ values to various adsorption isotherms. Temkin adsorption isotherm fits the experimental data. Plot of $\theta$ against log C for all concentrations of inhibitors Fig.(5) gives approximately a straight lines relationship. This suggests that the adsorption of 4-phenyl4-phenylthiazole derivatives on the $\alpha$-brass surface obeys Temkin adsorption isotherm Eq (5):

$$\ln KC = a\theta$$

where $K$ is the adsorption equilibrium constant and ‘$a$’ is the molecular interaction constant. The constant $fa$ depends on the intermolecular interaction in the adsorbed layer and on the heterogeneity of the surface. If ‘$a$’ is positive, mutual attraction of molecules occurs, if ‘$a$’ is negative repulsion occurs [27]. From the straight lines in the $\theta$ - log C graphs, equilibrium constants for the adsorption process, K, were obtained. The equilibrium constant is related to the free energy of adsorption, $\Delta G_{ads}$, by:

$$K = (1/55.5) \exp ( - \Delta G_{ads}/RT)$$

where 55.5 is the molar concentration of water in the solution in mol/L. The thermodynamic parameters for adsorption are given in Table 5. The values of $\Delta G_{ads}$ are negative which reveals the spontaneity of the adsorption process and the stability of the adsorbed layer on the brass surface. Since the value of $\Delta G_{ads}$ is less than -20 kJ mol$^{-1}$, this indicative of physisorption [28-30]. Moreover, the sign of ‘$a$’, is positive which indicates that the presence of attraction forces between the molecules of the adsorbed layer.

![Graph showing $\theta$ vs. log C curves for corrosion of $\alpha$-brass in 0.5 M HCl in the presence of different concentrations of all 4-phenylthiazole derivatives at 30 °C](image)

**Fig. 5** $\theta$ vs. log C curves for corrosion of $\alpha$-brass in 0.5 M HCl in the presence of different concentrations of all 4-phenylthiazole derivatives at 30 °C

3.5. Chemical structure of the inhibitors and corrosion inhibition

Skeletal representation of the proposed mode of adsorption of the investigated 4-phenyl4-phenylthiazole derivatives as shown in Fig. (6) and clearly indicates the active adsorption centers in the 4-phenyl4-phenylthiazole derivatives. These compounds can be adsorbed in a flat orientation through a bidentate form. The surface coordination is through the sulfur and the nitrogen atoms attached to the hetero ring. It was
concluded that the mode of adsorption depends on the affinity of the metal towards the π-electron clouds of the ring system [31]. This behavior can be rationalized on the basis of the structure-corrosion inhibition relationship of organic compounds. Linear Free Energy Relationships (LFER) has previously been used to correlate the inhibition efficiency of organic compounds with their Hammett constituent constants. The LFER or Hammett relation is given by [32-33]:

\[
\log R \text{ (corrosion rate)} = -\rho \sigma \tag{7}
\]

where \(\rho\) is the reaction constant. Those constituents which attract electrons from the reaction center are assigned positive \(\sigma\) values and those which are electron donating have negative \(\sigma\) values. Thus, \(\sigma\) is a relative measure of the electron density at the reaction center. The slope of the plot of \(\log (\text{rate})\) vs. \(\sigma\) is \(\rho\), and its sign indicates whether the process is inhibited by an increase or decrease of the electron density at the reaction center. The magnitude of \(\rho\) indicates the relative sensitivity of the inhibition process to electronic effects. Fig. (7) shows that 4-phenyl4-phenylthiazole derivatives (a-e) give a good correlation. The large positive slope of the correlation line \((\rho = +0.994)\) shows a strong dependence of the adsorption character of the reaction center on the electron density of the ring, with electron releasing substituents increasing inhibition. The strong dependence of the adsorption character of the reaction center on the electron density of the ring may be due to the fact that in this type of derivatives the center of adsorption is conjugated to the ring.

Compound (a) has the highest percentage inhibition efficiency, this due to the presence of p-OCH\(_3\) group which is an electron repelling group with negative Hammett constant \((\sigma = -0.27)\) this group will increase the electron charge density on the molecule. Compound (b) comes after compound (a), this is due to the presence of p-CH\(_3\) group which is an electron donating group with negative Hammett constant \((\sigma = -0.17)\). Also this group will increase the electron charge density on the molecule but with lesser amount than p-OCH\(_3\) group in compound (a). Compound (c) with Hammett constant \((\sigma = 0.0)\) comes after compound (b) in percentage inhibition efficiency, because H- atom in p-position has no effect on the charge density on the molecules. Compound (d) and (e) come after compound (c) in percentage inhibition efficiencies. This is due to both p-Br and p-NO\(_2\) groups are electron withdrawing groups with positive Hammett constants \((\sigma_{\text{Br}} = +0.23, \sigma_{\text{NO}_2} = +0.78)\) and their order of inhibition depends on the magnitude of their withdrawing character.

\[
\begin{align*}
(a) & \\
(b) & \\
(c) & \\
(d) & \\
(e) & 
\end{align*}
\]

Fig. 6 Skeletal representation of the mode of adsorption of 4-phenyl4-phenylthiazole derivatives
Conclusions
1. These compounds under investigation, the 4-phenyl-4-phenylthiazole derivatives, are fairly efficient inhibitors for \(\alpha\)-brass dissolution in 0.5 M HCl.
2. The adsorption of these compounds on \(\alpha\)-brass surface was found to obey Temkin's adsorption isotherm.
3. Galvanostatic polarization data indicated that, these inhibitors affect only the cathodic polarization and act as cathodic inhibitors.
4. The order of inhibition efficiency of all inhibitors as given by polarization measurements was explained on the basis of the chemical structure and adsorption active centers of the compounds.

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