INHIBITION OF CORROSION OF α-BRASS (Cu-Zn, 67/33) IN HNO₃ SOLUTIONS BY SOME ARYLazo INDole DERIVATIVES

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ABSTRACT

The influence of some arylazo indole derivatives on the corrosion rate of 70/30 α-brass in 2 mol l⁻¹ HNO₃ was investigated using weight loss and galvanostatic polarization techniques. It was found that the investigated compounds behave as inhibitors. The inhibition efficiency increases with increasing the inhibitor concentration, but decreases with increasing the temperature. The adsorption of these compounds on the α-brass surface follows a Frumkin’s adsorption isotherm. The electrochemical results indicated that all the investigated compounds act as mixed-type inhibitors. The influence of the substituent group on the inhibition efficiency of the inhibitor was explained in terms of the density of the electron cloud on arylazo indole moiety. Some thermodynamic parameters for corrosion and adsorption processes were determined and discussed.

Keywords: corrosion inhibition; α-brass; synergistic effect; HNO₃; arylazo indole derivatives.

INTRODUCTION

Copper and its alloys, because of their excellent resistance to corrosion in neutral aggressive media and their ease of processing, they are widely used in industries, particularly as condensers and heat exchangers in power plants[1]. Electrochemical techniques are powerful tools to study brass since they offer valuable information about the phase and chemical composition[2]. Such techniques have also proved to be useful to study the evolution of brass in the environment[3] to understand the degeneration process and to prevent oxidation of the alloy better[4].

A number of studies have recently appeared in the literature[5-8] on the topic of the corrosion inhibition of α-brass in acidic medium. But little work appears to have been done on the inhibition of α-brass alloys in HNO₃ using arylazo indole derivatives.

The aim of this paper is to describe an investigation of the inhibition of corrosion of commercial 67/33 brass in 2 mol l⁻¹ HNO₃ solutions by some arylazo indole derivatives using weight-loss and galvanostatic polarization measurements.

2. Experimental technique

2.1. Materials

The experiments were performed with local commercial α-brass (Helwan Company of Non-Ferrous Industries, Egypt) with the following composition (weight %) Cu 67.28, Pb 0.029, Fe 0.002, Zn 32.689. Brass specimens were employed in each experiment. The test pieces were cut into 20 x 20 x 2 mm. They were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), ultrasonically degreased in methanol, rinsed in doubly distilled water and finally dried between two filter papers and weighed. The test pieces were suspended ultrasonically degreased in methanol, rinsed in doubly distilled water and finally dried between two filter papers and weighed. The test pieces were suspended in the test solution, rinsed in doubly distilled water and finally dried between two filter papers and weighed. The test pieces were suspended in the test solution.

2.2. Electrochemical technique (galvanostatic polarization method):

The reaction basin used in this method was graduated glass vessel 6 cm inner diameter and having a total volume of 250 ml. 100 ml of the test solution was employed in each experiment. The test pieces were cut into 20 x 20 x 2 mm. They were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), ultrasonically degreased in methanol, rinsed in doubly distilled water and finally dried between two filter papers and weighed. The test pieces were suspended in the test solution.

2.3. Electrochemical technique (galvanostatic polarization method):

Three different types of electrodes were used during polarization measurements, the working electrode was α-brass electrode, which cut from the α-brass sheets, of thickness 0.2 cm. The electrode was of dimensions 1 cm x 1 cm and was weld from one side to a copper wire used for electric connection. The samples were embedded in glass tube using epoxy resin[11] the electrode was prepared before immersion in the test solution as in the case of weight loss. Saturated calomel electrode and a platinum coil as reference and auxiliary electrodes, respectively, were used. A constant quantity of the test solution (100 ml) was taken in the polarization cell. A time interval of about 30 min was given for the system to attain steady state. Both cathodic and anodic polarization curves were recorded galvanostatically using Amel galvanostat (Model 549) and digital multimeters (Fluke-73) were used for accurate measurements of the potentials and current density. All the experiments were carried out at 30 ±1°C by using an ultra circulating thermostat. The potential at any given current under similar experimental conditions was reproducible within ± 4%. Solutions were not deaerated to make the conditions identical to weight loss measurements.
RESULTS AND DISCUSSION

3.1. Weight-loss measurements

Figure (1) shows the weight loss-time curves for α-brass in 2 mol l\(^{-1}\) nitric acid in the presence and absence of different concentrations of compound (c) at 30°C. These curves are characterized by a sharp rise in weight loss from the beginning. Curves for additives containing system fall below that of the free acid. These curves indicated that the weight loss of α-brass depends on both the type and concentration of these additives. Increase in bulk concentration and consequently increase of surface coverage by the additive increases their inhibition efficiencies towards α-brass dissolution. The results of the Table (1) show that the inhibition efficiency of all additives increases with the increase of their concentrations in the corrosive medium. It is thus obvious that increase of bulk concentration and consequently, increase of surface area coverage by the additive retards the dissolution of α-brass. The order of the inhibition efficiency of the additive compounds in 2 mol l\(^{-1}\) HNO\(_3\) solution over most of the concentration ranges used after is.

![Weight loss-time curves for α-brass in 2 mol l\(^{-1}\) HNO\(_3\) in the presence and absence of different concentrations of compound (c) at 30°C.](image)

**Table (1):** Variation of the inhibition efficiency (% of the studied compounds with their molar concentrations after 120 min., immersion at 30°C.

<table>
<thead>
<tr>
<th>Concentration mol l(^{-1})</th>
<th>c</th>
<th>b</th>
<th>a</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x10(^{-6})</td>
<td>16.7</td>
<td>13.5</td>
<td>11.4</td>
<td>7.2</td>
</tr>
<tr>
<td>3x10(^{-6})</td>
<td>19.8</td>
<td>17.2</td>
<td>15.7</td>
<td>12.3</td>
</tr>
<tr>
<td>5x10(^{-6})</td>
<td>23.7</td>
<td>20.6</td>
<td>18.2</td>
<td>14.5</td>
</tr>
<tr>
<td>7x10(^{-6})</td>
<td>27.4</td>
<td>23.3</td>
<td>21.6</td>
<td>17.9</td>
</tr>
<tr>
<td>9x10(^{-6})</td>
<td>32.0</td>
<td>28.5</td>
<td>26.8</td>
<td>22.8</td>
</tr>
<tr>
<td>11x10(^{-6})</td>
<td>33.9</td>
<td>31.6</td>
<td>28.7</td>
<td>26.6</td>
</tr>
</tbody>
</table>

3.2. Adsorption isotherm

To understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the metal surface must be known\(^2\). The degree of surface coverage (q) which represents the part of metal surface covered by inhibitor molecules was calculated using the following equation:

\[
q = [1 – \left(\frac{W_{\text{inh}}}{W_{\text{free}}}\right)]
\]

(1)

where \(W_{\text{inh}}\) and \(W_{\text{free}}\) are the weight losses in the absence and in presence of inhibitors, respectively.

The degree of surface coverage was found to increase with increasing the concentration of the used additives. Attempts were made to fit q values to various isotherms including Frumkin, Freundlich, Langmuir and Temkin. By far, the best fit was obtained with Frumkin’s isotherm which has the following equation:

\[
q = \text{Const} + \left(\frac{2.303}{f}\right) \log C
\]

(2)

where, \(f= 1/RT \left[\frac{d(DG^o)}{dq}\right]\)

(3)

where C is the inhibitor concentration and \(DG^o\) is the free energy of adsorption. Fig. (2) represents the relation between q and log C for the inhibitors (a-d). The Frumkin’s adsorption isotherm is obeyed.

![Frumkin isotherm for the adsorption of investigated compounds on brass surface at 30°C, from weight loss method.](image)

3.3. Effect of temperature on the corrosion inhibition of α-brass

The dissolution of α-brass in 2 mol l\(^{-1}\) nitric acid increases by increasing temperatures Figure (3), the dissolution of α-brass in 2 mol l\(^{-1}\) HNO\(_3\) in the presence of different inhibitors at 11x10\(^{-6}\) mol l\(^{-1}\) was studied by weight loss method over a temperature range 30-50°C. The weight loss-time curves obtained (Figure 4) in the presence of additives indicate that the rate of α-brass dissolution increases as the temperature increases, but at lower rate than in uninhibited solutions. The inhibition efficiency of the additives decreases with rising the temperature which proves that the adsorption of these compounds on the surface of α-brass occurs through physical adsorption of the additives on the metal surface. Desorption is aided by increasing the reaction temperature. The apparent activation energy (E\(_a\)), the enthalpy of activation (ΔH\(_a\)) and the entropy of activation (ΔS\(_a\)) for the corrosion of α-brass in 2 mol l\(^{-1}\) nitric acid solution in the absence and presence of different concentrations of arylazo indole compounds were calculated from Arrhenius-type equation:
Rate \( k = A \exp(-E_a^*/RT) \)  

and transition-state equation:

Rate \( k = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \)  

where \((A)\) is the frequency factor, \((h)\) is the Planck’s constant, \((N)\) is Avogadro’s number and \((R)\) is the universal gas constant. Kinetic parameters obtained from plots of \( \log \text{Rate} \) vs. \( (1/T) \) [Fig. 5] and \( \log(\text{Rate}/T) \) vs. \( (1/T) \) [Fig. 6] graphs for the studied arylazo indole derivatives are given in Table (2). Inspection of Table 2 shows that higher values were obtained for \((E_a^*)\) and \((\Delta H^*)\) in the presence of inhibitors indicating the higher protection efficiency observed for these inhibitors. There is also a parallelism between increases in inhibition efficiency and increases in \((E_a^*)\) and \((\Delta H^*)\) values. The positive values of \((\Delta H^*)\) suggest that the dissolution process is an exothermic phenomenon and that the dissolution of \(\alpha\)-brass is difficult. Also, the entropy \(\Delta S^*\) widely decreases with the content of the inhibitor. This means the formation of an ordered stable layer of inhibitor on \(\alpha\)-brass surface 13.

**Fig. (3):** Weight loss-time curves for \(\alpha\)-brass dissolution in 2 mol l\(^{-1}\) HNO\(_3\) at different temperatures.

**Fig. (4):** Weight loss-time curves for \(\alpha\)-brass dissolution in 2 mol l\(^{-1}\) HNO\(_3\) in the presence of \((11 \times 10^{-6} \text{ mol l}^{-1})\) of compound (c) at different temperatures.

**Fig. (5):** Arrhenius plot for the corrosion of the \(\alpha\)-brass in 2 mol l\(^{-1}\) HNO\(_3\) in the presence and absence of investigated compounds.

**Fig. (6):** \(\log K/7\) vs. \(1/T\) for the corrosion of the \(\alpha\)-brass in 2 mol l\(^{-1}\) HNO\(_3\) in presence and absence of investigated compounds.
Values of inhibition efficiencies (In %) of different arylazo indole compounds in the presence of (1X10^{-2} mol l^{-1}) KSCN for the corrosion of α-brass in 2 mol l^{-1} HNO_3 at 30°C. Duration of the experiment: 120 min., immersion.

<table>
<thead>
<tr>
<th>Concentration, mol l^{-1}</th>
<th>c</th>
<th>b</th>
<th>a</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x10^{-6}</td>
<td>77.7</td>
<td>76.7</td>
<td>75.9</td>
<td>74.1</td>
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<td>75.7</td>
</tr>
<tr>
<td>5x10^{-6}</td>
<td>82.4</td>
<td>80.4</td>
<td>79.2</td>
<td>77.1</td>
</tr>
<tr>
<td>7x10^{-6}</td>
<td>84.4</td>
<td>82.9</td>
<td>80.9</td>
<td>78.4</td>
</tr>
<tr>
<td>9x10^{-6}</td>
<td>86.34</td>
<td>85.16</td>
<td>82.72</td>
<td>80.04</td>
</tr>
<tr>
<td>11x10^{-6}</td>
<td>88.29</td>
<td>86.73</td>
<td>84.32</td>
<td>81.57</td>
</tr>
</tbody>
</table>

Fig. (7): Weight loss-Time curves for α-brass in 2 M HNO_3 in the presence and absence of various concentrations of compound (c) and in presence of (1X10^{-2}M) of KSCN at 30°C.

where \( \theta_s \) = surface coverage by anion; \( \theta_a \) = surface coverage by cation; \( \theta\alpha \) = measured surface coverage by both the anion and cation. Table (4) shows the synergism parameter (S_\alpha) for constant KSCN concentration added to different concentrations of arylazo indole compounds. As can be seen from this Table, values nearly equal to unity were obtained, which suggests that the enhanced inhibition efficiencies caused by the addition of SCN^- to arylazo indole compounds is due mainly to the synergistic effect.

### 3.4. Synergistic effect

Some anions are found to enhance the inhibitive effect of several nitrogen containing organic compounds in acid solutions\textsuperscript{14-17}. In the present paper the influence of SCN^- ions on the inhibitive performance of arylazo indole compounds has been studied using weight loss technique. Figure (7) represents the weight loss-time curves for α-brass dissolution in 2 mol l^{-1} nitric acid for various concentrations of compound (c) at a concentration 1X 10^{-2} mol l^{-1} SCN^-.

The values of inhibition efficiency (In %) for various concentrations of inhibitors in the presence of specific concentration of KSCN are given in Table (3). The synergistic inhibition effect was evaluated using a parameter, \( S_\alpha \), obtained from the surface coverage values (\( \theta \)) of the anion, cation and both. Aramiki and Heckerman\textsuperscript{20} calculated the synergism parameter \( S_\alpha \) using the following equation:

\[
S_\alpha = 1 - \theta_1 - \theta_2 + \theta_1 \theta_2 \tag{6}
\]

The synergistic effect of this SCN^- anion has been observed by other authors\textsuperscript{21}. Adsorption of arylazo indole compounds at the α-brass/solution interface occurs through physical adsorption via electron rich centers, i.e. benzene ring through its π-electrons and nitrogen atoms through their lone pairs of electrons by donation of electrons to the empty d-orbital of the metal\textsuperscript{22}. It is known that SCN^- anions have strong interactions with \( \alpha \)-brass surfaces owing to chemisorptions\textsuperscript{22,23}. The strong chemisorptions of SCN^- anions on the metal surface are responsible for the synergistic effect of SCN^- anions in combination with cation of the inhibitor. The cation is then adsorbed by cumbic attraction on the metal surface where SCN^- anions are already adsorbed by chemisorptions. Stabilization of adsorbed SCN^- anions with cations leads to greater surface coverage and therefore greater inhibition.

### 3.5. Galvanostatic polarization technique

The cathodic and anodic polarization curves of α-brass in 2 mol l^{-1} nitric acid solution in the absence and presence of different concentrations of compound (c) at 30°C are shown in Figure (8). In the presence of inhibitor, the cathodic and anodic curves are shifted and the shift is dependent on inhibitor concentration. The polarization parameters such as corrosion current density (\( i_{corr} \)), Tafel slopes (\( \beta \)), percentage inhibition efficiency (In %), and degree of surface coverage (\( \theta \)) are listed in Table (5). As the concentration of the inhibitors increase, there is a marginal shift in \( E_{corr} \) and a decrease in \( i_{corr} \). The addition of inhibitors hinders acid attack on the \( \alpha \)-brass and a comparison of curves in both cases, shows that, with respect to the blank, increasing the inhibitor concentration gives rise to a consistent decrease in anodic and cathodic current densities, indicating that the arylazo indole derivatives act as mixed type inhibitors.
Fig.(8): Galvanostatic polarization curves of α-brass in 2 mol l⁻¹ HNO₃ alone and containing different concentrations of compound (c) at 30 °C.

Table (5): The effect of concentration of compound (c) on the free corrosion potential (Ecorr.), corrosion current density (icorr.), Tafel slopes (βa & βc), In % and degree of surface coverage (θ) for α-brass in 2 mol l⁻¹ HNO₃ at 30 °C.

<table>
<thead>
<tr>
<th>Concentration (mol l⁻¹)</th>
<th>In %</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>b</td>
</tr>
<tr>
<td>1x10⁻⁶</td>
<td>21.4</td>
</tr>
<tr>
<td>3x10⁻⁶</td>
<td>24.9</td>
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<tr>
<td>5x10⁻⁶</td>
<td>29.4</td>
</tr>
<tr>
<td>7x10⁻⁶</td>
<td>33.1</td>
</tr>
<tr>
<td>9x10⁻⁶</td>
<td>38.0</td>
</tr>
<tr>
<td>11x10⁻⁶</td>
<td>40.0</td>
</tr>
</tbody>
</table>

The values of cathodic Tafel slope βc for arylazo indole derivatives are found to change with inhibitor concentration, which clearly indicates that arylazo indole derivatives influence the kinetics of hydrogen evolution reaction. However, the values of the anodic Tafel slope βa increases only to small extent, as these compounds do not influence anodic dissolution. This indicates an increase in the energy barrier for proton discharge, leading to less gas evolution. The values of In % increase with increase in inhibitor concentration, indicating that a higher surface coverage was obtained in a solution with maximum concentration of inhibitor. The order of decreased inhibition efficiency of arylazo indole compounds is c > b > a > d (Table 6). This behavior can be rationalized on the basis of the structure-corrosion inhibition relationship of organic compounds. Linear Free Energy

Fig.(9): Frumkin isotherm for the adsorption of investigated compounds on brass surface at 30°C, from polarization method.

3.6. Chemical structure and corrosion inhibition of α-brass
Inhibition of the corrosion of α-brass in 2 mol l⁻¹ HNO₃ solution by some arylazo indole derivatives as determined by weight loss and galvanostatic polarization measurements was found to depend on concentration, nature of metal, the mode of adsorption of the inhibitors and surface conditions. Skeletal representation of the proposed mode of adsorption of the investigated arylazo indole derivatives as shown in Fig.(10) and clearly indicates the active adsorption centers in the arylazo indole derivatives. These compounds can be adsorbed through the N-atom of the pyridine ring. The surface coordination is through the nitrogen atoms. It was concluded that the mode of adsorption depends on the affinity of the metal towards the π-electron clouds of the ring system. Metals such as Cu and Fe, which have a greater affinity towards aromatic moieties, were found to adsorb benzene rings in a flat orientation. Thus, it is reasonable to assume that the tested inhibitors are adsorbed in a flat orientation through the N-atom of the pyridine ring and O-atom of the OCH₃ group as shown in Fig.(11). The order of decreasing the inhibition efficiency of the investigated compounds in the corrosive solutions was as follows: c > b > a > d. This behavior can be rationalized on the basis of the structure-corrosion inhibition relationship of organic compounds. Linear Free Energy
Hammett constants, $\sigma$ of inhibition depends on the magnitude of its withdrawing character. Compound $p$ has the highest percentage inhibition efficiency, this due to the presence of $p$-NO$_2$. The LFER or Hammett relation is given by:

$$\text{Log}\ R = -\rho \sigma$$  \hspace{1cm} (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 (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. Figure (11) shows that indole derivatives (a-d) give a strong 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. 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 (c) 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 (c), 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 (c). Compound (a) 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) comes after compound (a) in percentage inhibition efficiencies. This is due to $p$-NO$_2$ groups is electron withdrawing group with positive Hammett constants ($\sigma = +0.78$) and its order of inhibition depends on the magnitude of its withdrawing character.

![Fig.10](image-url)  \hspace{1cm} \text{Skeletal representation of the mode of adsorption of indole compounds. $\sigma_p$ (Substituent constant)}

Relationships (LFER) has previously been used to correlate the inhibition efficiency of organic compounds with their Hammett constituent constants ($\sigma$) \cite{25,26}. The LFER or Hammett relation is given by:

$$\text{Log}\ R = -\rho \sigma$$  \hspace{1cm} (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 (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. Figure (11) shows that indole derivatives (a-d) give a strong 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. 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 (c) 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 (c), 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 (c). Compound (a) 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) comes after compound (a) in percentage inhibition efficiencies. This is due to $p$-NO$_2$ groups is electron withdrawing group with positive Hammett constants ($\sigma = +0.78$) and its order of inhibition depends on the magnitude of its withdrawing character.

![Fig.11](image-url)  \hspace{1cm} \text{Relation between log corrosion current density, log $i_{corr}$, and Hammett constants, $\sigma_p$ of the substituent from polarization measurements.}

**REFERENCES**