Effect of copper cation on corrosion of steel by tolytriazole in acid medium

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The influence of different concentrations of tolytriazole in the presence of 0.1M sulphuric acid on electrochemical and corrosion behaviour of steel both with and without different concentrations of copper cation was studied potentiokinetically. It was found that tolytriazole reduces the corrosion current, corrosion rate and increases the polarization resistance. The protective cation was incorporated into the protective layer formed on the electrode surface exposed to tested solution. It was found that at a concentration of 10^{-1} M, Cu^{+} cation strongly inhibited the corrosion rate rather than at lower cation concentration. The corrosion of the steel in 0.1M H_2SO_4 is appreciably reduced by tolytriazole in combination with metallic copper cation, as a result of coadsorption. The corrosion potential, corrosion current, corrosion rate, polarization resistance, as well as activation energy and thermodynamic parameters were calculated at different temperatures.

In most inhibition studies the formation of donor-acceptor surface complexes between free or pi-electrons of an inhibitor and vacant d-orbital of a metal were postulated. Nitrogen compounds have also been studied as inhibitors. Metallic cations such as ions of common metal present in acid solutions have been studied with regard to corrosion process and hydrogen absorption by steel. Gatos has mentioned that oxidizing ions (Fe^{+++}, Cu^{++}) increases the corrosion rate of iron linearly in 1N H_2SO_4, 1N HCl, and 1N acetic acid. The anion of the inhibitor can function either by favouring the passivation reaction or by promoting the formation of a protective physical barrier to the ingress of electrolyte. Examination of Pourbaix potential-pH diagram indicate that many cations formed in soluble hydroxide and oxides at pH values in excess of 8 for a potential range appropriate to oxygen reduction and therefore may be expected to inhibit the corrosion of iron. Recently it was found that the presence of Zn^{++}, Cd^{++} and Mn^{++} cations inhibits the hydrogen evolution reaction on iron in acid medium. As discussed by Licht et al., cationic relation effects might be expected to occur in the electrode/electrolyte interfacial region. Since cations are not directly involved in charge-transfer processes, they may not only modify anion activity, but can also alter the physical and electrical structure of the inner and outer Helmholtz planes (IHP and OHP) and thereby affect both the potentials and the charge transfer in the interfacial region. Although cations are not directly involved in the redox reactions they do, however, provide indirect influence on the electrode phenomenon.

In the present research work, the corrosion inhibition of steel in H_2SO_4 acid by the addition of tolytriazole with and without CuSO_4 has been studied.

Experimental Procedure

The specimens of the steel samples were machined into rectangle form, 1.8 cm in length and 1 cm in width. They were inserted in Teflon in such a way that the flat surface was in contact with the solution. Preparation of the electrode surface was prepared as described previously. A stock of the copper cation and tolytriazole were prepared and required concentration was prepared and diluted with the tested solution. The detail of the cell used in the investigation was described earlier. A conventional three electrode system was used. Carbon rod electrode was used for the auxiliary electrode, the working electrode was a steel, the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary.

Potentiodynamic studies were performed using a corrosion measurement system, (model 273 EG & G corrosion software potentiostat/galvanostat). The anodic and cathodic polarization curves were obtained at a scan rate of 2 mV s^{-1} and the potential range from -1000 to +600 mV. The electrochemical parameters of this study were obtained from the potentiokinetic polarization curves at 30 - 65 °C. These include the corrosion potential, corrosion current, corrosion rate and polarization resistance and also determination of thermodynamic functions ΔΗ, ΔG, ΔS and E.

An average of the data for five independent runs was collected. Runs in which three or more of the
electrochemical parameters were out of one standard deviation from their sample average were discarded.

For studying the effect of the tested cation, the test was conducted in 0.1M sulphuric acid, with the desired amount of the inhibitors and the metallic cation added. The stock solution of the inhibitor and the metallic cation were in 0.1M sulphuric acid before the experiment started.

**Results and Discussion**

Sulphuric acid (0.1M) containing various concentrations of tolytriazole was used for potentiodynamic measurements. The polarization curves for these solutions at 30 °C are shown in Fig. 1(a-d). From this figure it is clear that $10^{-2} \text{M}$ tolytriazole show no primary and secondary passivity, but at higher concentration of tolytriazole ($5 - 9 \times 10^{-2} \text{M}$) show primary and secondary passivity. Anodic and cathodic Tafel slopes are required for calculating the corrosion rate using the linear polarization data for inhibited as well as uninhibited solutions (Table 1). Anodic and cathodic Tafel slopes are usually reported to be in the range $B_a/B_c = 70/120$ to 110/190$^{18,21}$. By using the Stern-Geary equation:

$$I(\text{mAcm}^{-2}) = \frac{B_pB_c/(2.3(B_a+B_c))}{R}$$

The value in the bracket is the $B$ constant and $R_p$ is the polarization resistance generated by the linear polarization scan. The corrosion rate was calculated from linear polarization technique, (Table 2). All the values reported were obtained from triplicate experiments. Since corrosion rate is directly related to corrosion current, the inhibition efficiency (P%) at different concentrations and temperatures for tolytriazole can be calculated from the equation.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ ($\mu$A cm$^{-2}$)</th>
<th>$B_a$ (mV)</th>
<th>$B_c$ (mV)</th>
<th>$R_p$ ($\Omega$ cm$^2$)</th>
<th>$B$ (MV)</th>
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<tr>
<td>Blank</td>
<td>518</td>
<td>578.4</td>
<td>100</td>
<td>100</td>
<td>2.559</td>
<td>21.73</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$</td>
<td>466</td>
<td>78.83</td>
<td>103</td>
<td>98</td>
<td>3.849</td>
<td>21.83</td>
</tr>
<tr>
<td>$6 \times 10^{-2}$</td>
<td>466</td>
<td>4961</td>
<td>100</td>
<td>100</td>
<td>3.975</td>
<td>22.05</td>
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<td>$7 \times 10^{-2}$</td>
<td>291</td>
<td>4199</td>
<td>105</td>
<td>97</td>
<td>4.396</td>
<td>21.82</td>
</tr>
<tr>
<td>$9 \times 10^{-2}$</td>
<td>181</td>
<td>3.97</td>
<td>99</td>
<td>97</td>
<td>5.286</td>
<td>21.30</td>
</tr>
</tbody>
</table>

Table 1 - Corrosion potential $E_{corr}$ (mV), corrosion current density $i_{corr}$ ($\mu$A cm$^{-2}$), polarization resistance ($R_p$ $\Omega$ cm$^2$) and anodic and cathodic Tafel slopes ($B_a/B_c$) (mV) of steel in 0.1M sulphuric acid at different concentrations of tolytriazole versus SCE at 30 °C.

<table>
<thead>
<tr>
<th>Tolytriazole M</th>
<th>Corrosion current ($\mu$A cm$^{-2}$)</th>
<th>Protection efficiency (P%)</th>
<th>Corrosion rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>39.9</td>
<td>-</td>
<td>12.22</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$</td>
<td>9.8</td>
<td>75.43</td>
<td>3.003</td>
</tr>
<tr>
<td>$5 \times 10^{-2}$</td>
<td>4.678</td>
<td>88.28</td>
<td>1.8198</td>
</tr>
<tr>
<td>$7 \times 10^{-2}$</td>
<td>3.645</td>
<td>90.86</td>
<td>1.098</td>
</tr>
<tr>
<td>$9 \times 10^{-2}$</td>
<td>5.433</td>
<td>91.39</td>
<td>1.051</td>
</tr>
<tr>
<td>Blank</td>
<td>182.6</td>
<td>-</td>
<td>190</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$</td>
<td>152</td>
<td>70.52</td>
<td>54</td>
</tr>
<tr>
<td>Blank</td>
<td>240.8</td>
<td>-</td>
<td>73.73</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$</td>
<td>222</td>
<td>65.67</td>
<td>77.5</td>
</tr>
</tbody>
</table>

Table 2 - Values of corrosion rates, corrosion current and protection efficiency (P%) calculated by the Linear polarization tests
Fig. 2—Plots of log \((0 / 1 - \theta)\) versus log C at 30 °C for \(10^{-2}\) M tolytriazole

\[ P\% = \frac{[i_a - i_c]}{i_a} \times 100 \]  

... (2)

where \(i_a\) and \(i_c\) are the corrosion rates in uninhibited and inhibited solutions respectively. Table 2. Also, the degree of coverage, \(\theta\), at constant potential is given by\(^{23-24}\):

\[ \theta = \frac{[i_a - i_c]}{i_a} \]  

... (3)

The inhibition efficiency was calculated from linear polarisation results. At lower inhibitor concentration, the protection is generally less than that at a higher concentration. Since the efficiency decreases with the increase in temperature, it is effective at lower temperature. The protection efficiencies were found to have 86.37, 72 and 59 for \(10^{-2}\) tolytriazole in 0.1 M sulphuric acid solution at 30, 45 and 65 °C respectively. If it is assumed that tolytriazole forms a monolayer adsorption over steel surface, then at any instance the fraction of the surface covered and not exposed to corrosion medium is equal to \((i_a - i_c)/i_a\) within a certain range of inhibitor and temperature where monolayer adsorption is readily maintained over the steel surface Fig.2.

Fig. 2 represents the Langmuir adsorption isotherm which may be expressed from the equation.

\[ \frac{\theta}{(1 - \theta)} = AC \exp \left( -\frac{Q}{RT} \right) \]  

... (4)

where \(A\) is a constant, \(C\) is inhibitor concentration, \(Q\) is the heat of adsorption, \(\theta\) is the occupied and \((1 - \theta)\) is the vacant sites not occupied by the inhibitor. The equation can be represented in the form

\[ \log \left[ \frac{\theta}{(1 - \theta)} \right] = \log A + \log C - \frac{Q}{2.3RT} \]  

... (5)

Fig. 3—Plots of log \((0 / 1 - \theta)\) versus \(1/T\) at different temperatures for \(10^{-2}\) M tolytriazole.

Fig. 4—Effect of temperature on polarization curves of steel in 0.1 M sulphuric acid in presence of \(10^{-2}\) M tolytriazole

(a) 30 °C, (b) 45 °C, (c) 65 °C
Table 3—Effect of different temperatures on corrosion potential $E_{corr}$ (mV), corrosion current $i_{corr}$ ($\mu$A cm$^{-2}$) polarization resistance $R_p$ ($\Omega$ cm$^2$), and cathodic and anodic Tafel slopes ($B_c$, $B_a$) of steel for $10^{-2}$ M tolytriazole.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$E_{corr}$ mV</th>
<th>$i_{corr}$ $\mu$A cm$^{-2}$</th>
<th>$B_c$ mV</th>
<th>$B_a$ mV</th>
<th>Polarization resistance $R_p$ ($\Omega$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C</td>
<td>518</td>
<td>177.1</td>
<td>100</td>
<td>100</td>
<td>2.559</td>
</tr>
<tr>
<td>Blank</td>
<td>466</td>
<td>78.83</td>
<td>103</td>
<td>98</td>
<td>3.849</td>
</tr>
<tr>
<td>45 °C</td>
<td>525</td>
<td>182.6</td>
<td>112</td>
<td>87</td>
<td>1.955</td>
</tr>
<tr>
<td>Blank</td>
<td>485</td>
<td>152</td>
<td>108</td>
<td>86</td>
<td>1.994</td>
</tr>
<tr>
<td>65 °C</td>
<td>550</td>
<td>240.8</td>
<td>118</td>
<td>62</td>
<td>1.031</td>
</tr>
<tr>
<td>Blank</td>
<td>520</td>
<td>222</td>
<td>138</td>
<td>85</td>
<td>1.185</td>
</tr>
</tbody>
</table>

Table 4—Activation energy $E$, $\Delta G$, $\Delta H$ and temperature coefficient for the adsorption of $10^{-2}$M tolytriazole on steel surface.

<table>
<thead>
<tr>
<th>$E$ (kJ mol$^{-1}$)</th>
<th>$-\Delta G$ (kJ mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$ M)</th>
<th>Temperature coefficient ($\frac{\Delta E}{\Delta T}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67.29</td>
<td>26.456</td>
<td>69.93</td>
<td>1.64 x 10$^6$</td>
</tr>
<tr>
<td>30 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To test the conformity of these results with this simple model, [log $\theta^{(1-\theta)}$] against log $C$ was plotted, which gives a straight line with unit gradient. Fig. 2 shows that the results fit in with straight line. However, the gradient is less than unity (0.55). Such a discrepancy may be explained on the premise that a considerable area of holes is left through which Fe$^{2+}$ ions can still pass. Graham$^5$ pointed out that the Langmuir constant A (slope of the straight line, Fig.2) which he named the equilibrium function, can possibly be less than unity for adsorption on heterogeneous surfaces in general and much smaller than unity when there is no lateral interaction between the adsorbate molecules. A plot of log[log $\theta^{(1-\theta)}$] against $1/T$ at constant concentration of tolytriazole is shown in Fig. 3. The slope of the curve in Fig. 3 is equal to $-Q/2.3R$ and heat of adsorption is equal to 50.95 kJ mol$^{-1}$.

Effect of temperature

The effect of temperature on the inhibition efficiency was determined for 0.1M sulphuric acid containing $10^{-2}$ M of tolytriazole at different temperatures ranging from 30 - 65 °C (Fig.4), and the results are given in Table 3.

Potentiodynamic polarization studies for steel in presence of $10^{-2}$ M tolytriazole show no primary and secondary passivity at 30 °C, but at 45 and 65 °C show primary and secondary passivity. The increase in temperature cause a slight increase in the active and passive regions. The increase in active region can be attributed to the desorption of tolytriazole on the electrode surface, where sulphuric acid enhance the anodic dissolution. The increase in the passive region could be attributed to the slight penetration of the passive film by the aggressive sulphate ions. The inhibition efficiency was found to decrease with increasing temperature from 30 to 65 °C. The values of the activation energy $E_a$ were calculated from the equation.

$$E = -2.32(1.987)(4.18) \frac{d(log I)}{d(1/T)} \text{ KJ mol}^{-1} \quad \cdots (6)$$

The plot of logarithm of the corrosion rate versus $1/T$ are given in Fig. 5. The $E_a$ values are given in Table 4. It is evident that for the corrosion of steel in 0.1M sulphuric acid, the $E_a$ values were found to equal 38.45 kJ mol$^{-1}$ and for tolytriazole which function as effective inhibitor, the $E_a$ values are higher, and equal 67.29 kJ mol$^{-1}$. According to Machu$^6$ the kinetics of such a corrosion process acquire the character of a diffusion process, in which
at lower temperature the quantity of inhibitor present at the metal surface is greater than that at higher temperatures. The values of the free energy of adsorption $\Delta G$ can be calculated using the following equation.

$$KC = \frac{\theta}{(1-\theta)}$$  \hspace{1cm} (7)

$$K = \frac{1}{55.5} \exp\left[-\frac{\Delta G}{RT}\right]$$  \hspace{1cm} (8)

and are given in Table 4. The results show that $9 \times 10^{-2}$ M of tolytriazole gives a maximum efficiency at 30 °C (Table 2). And shows a more negative free energy of adsorption (Table 5), indicating that it is strongly adsorbed on a steel surface. Enthalpy of tolytriazole adsorption on steel surface can be deduced from the equation\(^2\).

$$E = \Delta H - RT$$  \hspace{1cm} (9)

Mechanism of inhibition

Tollytriazole is a heterocyclic compound with a nitrogen atom forming part of the ring. Owing to the acidity of the medium, the basic compound cannot remain in solution as free as base, and it may therefore be assumed that at least in the first few moments of contact between the metal and the solution, it exist at the interface in the cationic form, attached to the anodic points; it is also possible that the alkalinity produced at the cathodic sites favours the free base, which would then be generally adsorbed on the metal surface. The linearity of the plot of log [\(\theta / (1- \theta)\)] versus the inhibitor concentration suggests that the tolytriazole undergo anodic adsorption of the Langmuir isotherm.

The inhibitor used in this work is classified as a toxic substance and can inhibit the catalytic activity of a metal surface owing to the presence of the lone pair of electrons on nitrogen atoms\(^28\). The poisoning effect results from the formation of strong bonds between the inhibitor molecule and cathodic surface atoms. This conclusion agrees well with the calculated values (Table 4) of $\Delta H$, as the heat of adsorption is known to be a good measurement of the strength of adsorption on a surface.

The temperature coefficient of the inhibited acid corrosion depends on the concentration of the inhibitor\(^2\) and can be calculated from Eq.\((10)\)

$$\Delta G = \Delta H - ZF \left(\frac{dE}{dT}\right)$$  \hspace{1cm} (10)

The temperature coefficient for corrosion inhibition has a positive value (Table 4), which may be explained by assuming that the corrosion reaction is no longer the simple metal/acid reaction, but involves the adsorbed species directly.

Effect of metallic copper cation on inhibition efficiency

As mentioned by Licht et al.\(^15\), cations related effects might be expected to occur in the electrode/electrolyte interfacial region. Since cations are not directly involved in charge-transfer process, they may modify anion activity, and can alter physical and electrical structure of the inner and outer Helmholtz planes and thereby affect both the potentials and the charge transfer in the interfacial region. It is clear from Fig. 6 that metallic copper cation maximized corrosion inhibition at a higher concentration, but at a lower concentration, the inhibition efficiency decreased. Maximum inhibition efficiency was obtained with $10^{-1}$ M Cu$^{+}$ ion and was found to be 96.69%. The inhibition efficiency of tolytriazole at a concentration of $10^{-2}$ M in 0.1M

<table>
<thead>
<tr>
<th>Conc. of Cu cation (M)</th>
<th>Corrosion potential (mV versus SCE)</th>
<th>Corrosion rate (mpy)</th>
<th>Protection efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-1}$</td>
<td>-487.1</td>
<td>9.405</td>
<td>96.14</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$</td>
<td>-485</td>
<td>10.64</td>
<td>95.63</td>
</tr>
<tr>
<td>$1 \times 10^{-3}$</td>
<td>-483</td>
<td>12.27</td>
<td>94.96</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>-472.5</td>
<td>24.88</td>
<td>85.95</td>
</tr>
</tbody>
</table>
H₂SO₄ containing no metallic cation were found to be 86.37%. The corrosion rate results in 0.1M sulphuric acid containing tolytriazole and varying concentrations of tested cation are reported in Table 5 and plotted in Fig. 7. From Figs 6 and 7, it is clear that the inhibition efficiency of tolytriazole increases and the corrosion rate decreased with the increase in the concentrations of metallic copper cation. At lower concentration of Cu²⁺ion (10⁻⁴ M) inhibition efficiency of tolytriazole-copper combination were found to decrease steadily to inhibition values below that observed when only addition of tolytriazole was used (Fig.6).

**Effect of the copper cation on the corrosion potential**

The effect of metallic copper cation on the corrosion potential is plotted in Fig. 8. It is clear that the potential shifts to the electronegative direction, with an increase in concentration of copper cation.

The inhibition of corrosion by the presence of the metallic copper cation may be a result of adsorption / electrodeposition of the cation on the electrode surface. The nitrogen atom in the tolytriazole molecule help in anchoring the molecule on the steel surface. The increase of the inhibition efficiency of tolytriazole in the presence of (10⁻¹ M) copper cation is attributed to the co-adsorption of the inhibitor and metallic copper cation on the steel surface. Anoshchenko²⁹ and Vorkapic³⁰ have also proposed that a reduction of corrosion rate of steel in sulphuric acid, in the presence of cations, is a consequence of the adsorption of the cations. The increase in inhibition efficiency at higher concentrations of the metallic copper cation in the presence of tolytriazole may be owing to the represented cathodic reaction, resulting in lower deposition of metal on the electrode surface in preference to the co-adsorption of the inhibitor and metallic copper cation. The deposited metal either adherent or loose may therefore result in localized corrosion caused by galvanic action. At lower concentration of copper cation (10⁻⁴ M) in association with tolytriazole, an increase in the corrosion rate is observed.

Singh³¹ found that the addition of Cu⁺⁺, Hg⁺⁺ and Ce⁺⁺ in low concentrations to steel electrodes, poisons or decatalyzed hydrogen evolution reaction by co-joint adsorption, and lowering the exchange current density for hydrogen will produce a lower corrosion rate and shift the open circuit potential in the electronegative direction. The addition of copper cation (10⁻⁴M) in the presence of tolytriazole decreases the corrosion rate and shifts the open circuit potential in an electropositive direction as compared...
with $10^{11}$ M copper cation. The shift of the potential towards more electropositive values may be owing to suppression of the reduction of $\text{H}^+$ ions. As a result, the reduction of the metallic cation becomes the predominant cathodic reaction, leading to the deposition of the metal. The deposited metal thereby increases the corrosion rate.

Other postulations that may account for these effects include a surface blocking effect, which reduces the quantity of bare iron sites for active corrosion, but promoted localized attack at bare sites.

References