Corrosion Inhibition of Copper in 3% NaCl Solution by Derivative of Aminotriazole

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ABSTRACT

The inhibiting effect of N-decyl-3-amino-1,2,4-triazole (TN₁₀) against Copper corrosion in aerated 3% NaCl, has been developed. Potentiodynamic measurements and electrochemical impedance spectroscopy have been applied to determine the corrosion rate. Scanning electron microscopy (SEM) studied surface morphology has been also used to characterize electrode surface. The obtained results indicate that TN₁₀ acts as a good mixed-type inhibitor retarding both anodic and cathodic reactions. An increase of TN₁₀ concentration leads to a decrease of corrosion rate and inhibition efficiency increase.

Keywords: Copper, Triazole, 3% NaCl Solution, Corrosion, Inhibition

1. Introduction

Due to its high electrical and thermal conductivity and good mechanical workability, copper is a material widely used in pipelines for domestic and industrial water utilities, including sea water, heat conductors, and heat exchangers [1]. In spite of the relatively noble potential of copper, its corrosion takes place at a significant rate in sea water and chloride environments [2-9]. It is generally accepted that the anodic dissolution of copper in chloride environments is influenced by the chloride ions concentration. At chloride concentrations lower than 1 M, the dissolution of copper occurs through the formation of CuCl, which is not protective enough and is converted to the soluble CuCl₂ by reacting with excess chloride [10].

Heterocyclic compounds, especially nitrogen-based ones, are effective inhibitors, being coordinate with Cu(0), Cu(I) or Cu(II) via their nitrogen atoms through lone pair electrons to form polymeric complexes with copper [11-17]. These form an adsorbed protective film on the copper surface, providing inhibition of corrosion by acting as a barrier to aggressive ions such as chloride [18-20]. Polar functional groups such as nitrogen, sulfur, and oxygen and conjugated double bonds are considered reaction centers in establishing the adsorption process [21,22]. In others previous work, the influence of organic compounds on the corrosion of copper in neutral solution have been studied [23-28].

The present investigations discusses the results obtained in studying the corrosion behavior of pure copper in aerated 3% NaCl solution in absence and in presence of an aminotriazole derivative like N-decyl-3-amino-1,2,4-triazole noted (TN₁₀). The electrochemical methods and surface characterization have been used to characterize the inhibiting effect.

2. Experimental Conditions

A classic electrochemical cell with three-electrode configuration was used in this study: a platinum grid as a counter electrode, a rotating disk of pure copper (99.9%) as working electrode, and Ag/AgCl in 3 M KCl (SSE) as a reference one.

The working electrode was made of cylinder rod of pure copper (Goodfellow) of 12.5 mm in diameter. A cylinder rod of about 1 cm height was fixed to a stainless-steel shaft, and then the lateral part was covered with a cataphoretic epoxyamine base paint (PPG; WT724 + P962). First, the paint was deposited at a constant voltage of 180 V during 4 min, and then cured at 180°C for 30 min. After that, the electrode was embedded into an epoxy resin (Buhler; Epoxycure), and worked out to the cylinder shape, the outer diameter was 21 mm. Only the cross-section of the alloy rod embedded in the epoxy resin was used to form a rotating disk electrode. The cataphoretic coating allowed avoiding any infiltration of electrolyte between the metal and epoxy resin interface.
Just before each experiment, the electrode surface was polished by emery-paper up to 1000 grit. The corrosive solution was prepared with distilled water and reagent grade chemicals of NaCl. We obtain 3% of NaCl solution.

The potentiodynamic measurements were performed using a PG201 potentiostat/galvanostat. The electrode was immersed for 1h in the test solution in free corrosion conditions. Then, the polarization curves were recorded by changing stepwise (60 mV/min) the potential.

Impedance (EIS) measurements were done using an EG&G apparatus (model 6310), with a frequency interval ranging from 100 kHz to 10 mHz.

The surface morphology of the electrode was performed by using scanning electron microscope (SEM).

3. Results and Discussion

3.1. Voltammetry Experiments

The cathodic and anodic polarization curves of the copper obtained with a RDE at 1000 rpm in 3% NaCl solution with various TN10 concentrations are presented in Figures 1 and 2, respectively. The range of TN10 concentrations investigated in this work between 10⁻⁴ M and 10⁻⁻³ M. All of these curves were obtained after 1 h immersion of the electrode in the electrolytic solution at open-circuit corrosion potential (Ecorr). Then cathodic and anodic polarization curves were recorded from independent experiments. The initial potential was stated at a slightly more positive potential from Ecorr for the cathodic scans, and conversely, it was set at a slightly more negative value from Ecorr for the anodic scans.

In absence of TN10, the cathodic current (Figure 1) follows the Tafel law for E > −0.6 V/SCE, and then the corrosion current density can be determined readily after diffusion correction (icorr ≈ 127 μA/cm²). For potential more negative than −0.6 V/SCE, the current plateau observed is ascribed to the limiting current of the dissolved oxygen reduction. The adding of 0.05 mM or 0.1 mM of TN10 into the corrosive medium is accompanied by both a shift of Ecorr toward more positive potential, and a decrease of i corr.

It is important to point out that for potential more positive than −0.4 V/SCE, the Tafel slope is independent of the inhibitor concentration. In contrast, the cathodic curves in the most negative potential domain (Figure 1) are different in presence and absence of TN10, namely, the limiting diffusion current corresponding to the oxygen reduction is always observed. This may be explained, for instance, by the formation of surface film which hinders the diffusion of dissolved oxygen towards the electrode surface in addition to the hydrodynamic diffusion layer.

The extrapolation of cathodic polarization curve to the open-circuit corrosion potential Ecorr allowed evaluating the corrosion current density. The results are summarized in Table 1. The inhibiting efficiency E in percent was calculated according to the following expression:

\[
E = 100 \frac{i_{corr} - i_{corr}}{i_{corr}}
\]

where \(i_{corr}\) and \(i_{corr}\) denote the corrosion currents densities in absence and in presence of inhibitor, respectively.

The inhibiting efficiency increases with the TN10 concentration for a given temperature and immersion time, and it reaches 99.2% for the addition of 1 mM of TN10.

In absence of inhibitor, the anodic curve (Figure 2) exhibits two distinct domains: the first zone is located in the vicinity of the corrosion potential and is characterized by a steep Tafel slope whereas the second zone located towards more positive potentials is characterized by a quite constant current density. This limiting current density is likely governed by the solubility of CuCl₂ salt layer as mentioned elsewhere [29].

The anodic polarization curves change dramatically by

### Table 1. Corrosion inhibition parameters of cooper in aerated 3% NaCl solution without and with addition of TN10 at various concentrations at 25°C.

<table>
<thead>
<tr>
<th>C, TN10 (M)</th>
<th>b_i (mV/dec)</th>
<th>E_corr (mV)</th>
<th>I_corr (μA/cm²)</th>
<th>E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>−239</td>
<td>−260</td>
<td>5.7</td>
<td>-</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>−262</td>
<td>−248</td>
<td>1.26</td>
<td>77.9</td>
</tr>
<tr>
<td>5 × 10⁻⁴</td>
<td>−260</td>
<td>−238</td>
<td>1</td>
<td>82.5</td>
</tr>
<tr>
<td>10⁻³</td>
<td>−323</td>
<td>−191</td>
<td>0.27</td>
<td>95.3</td>
</tr>
<tr>
<td>5 × 10⁻⁴</td>
<td>−234</td>
<td>−180</td>
<td>0.087</td>
<td>98.5</td>
</tr>
<tr>
<td>10⁻³</td>
<td>−247</td>
<td>−142</td>
<td>0.047</td>
<td>99.2</td>
</tr>
</tbody>
</table>
addition of TN$_{10}$. This change is accompanied by a significant decrease of the anodic current density which is more marked near $E_{\text{corr}}$, and an apparition of large passive domain. This later is clearly observed for various concentrations of TN$_{10}$. For instance, at $-0.1$ V/SCE and $-0.15$ V/SCE, the inhibitory efficiency E(%) is respectively about 99.7%, 99.92% and about 99.99% for 0.01 mM, 0.1 mM and 1 mM of TN$_{10}$ respectively. These effects can be explained by the fact that the product tested acts by adsorption on the surface of the material and contributes to an establishment of an inhibiting film relatively compact.

But at higher electrode polarization, the presence of TN$_{10}$ seems to have low effect, because the anodic current density values are sensibly equal to those obtained without inhibitor. This may be attributed to inhibitor film desorption [30,31] or its destruction under anodic reactions like sample and water oxidations coming under the inhibitor film and in surface sites identified.

Figure 3 shows the curve $\theta = E_{\text{corr}}/100$, as a function of log concentration $C$ of TN$_{10}$ where $\theta$ is the surface coverage. The TN$_{10}$ adsorbs on the copper surface according to the Frumkin isotherm model, which is given by the general equation:

$$\frac{\theta}{1 - \theta} e^{\theta} = \frac{C}{55.5} e^{rac{-\Delta G_{\text{ads}}}{RT}}$$

(2)

where $\Delta G_{\text{ads}}$, the free energy of adsorption, is equal to 37.42 kJ/mol.

The obtained results show that the TN$_{10}$ inhibit both the cathodic and anodic processes. It acts as a mixed type inhibitor.

3.2. Electrochemical Impedance Spectroscopy (EIS)

The impedance diagrams are represented in Nyquist plot, obtained in solution without and with $10^{-3}$ M of TN$_{10}$ inhibitor, are presented in Figure 4. The electrode was immersed in solution at the free corrosion potential until a steady-state was attained.

In the absence of TN$_{10}$, one capacitive loop is clearly observed with dispersion in low frequencies range. The associated resistance value is about 2620 kOhm·cm$^2$, the corresponding capacity value is in the order of 96 $\mu$F/cm$^2$. This loop may be attributed to a charge transfer process, occurring on the copper surface. In the same figure we note that the impedance display of the electrode in TN$_{10}$ containing solution changes in shape and size. On the other hand it can be noticed that the impedance modulus increased dramatically in presence of inhibitor at $10^{-3}$ M concentration. The presence of two capacitive loops seems to indicate a diffusion contribution to the beginning of the experiment. At high frequency loop, it is found that the resistance value increased in the presence of inhibitor, whereas the double layer capacity value found to be decreased (Table 2). The decrease of capacity value was due to the adsorption of inhibitor.

Figure 4. Electrochemical impedance spectra of copper in aerated NaCl 3% without and with $10^{-3}$ M of TN$_{10}$ at 25°C: $\Omega = 1000$ rpm.
Table 2. Impedance measurements and inhibition efficiency on copper in 3% NaCl solution without and with 10^{-3} M of TN_{10}.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>R_{t} (k\Omega \cdot \text{cm}^2)</th>
<th>C (\mu\text{F/cm}^2)</th>
<th>f (Hz)</th>
<th>E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% NaCl</td>
<td>2,620</td>
<td>96</td>
<td>0.63</td>
<td>-</td>
</tr>
<tr>
<td>3% NaCl + 10^{-3} M TN_{10}</td>
<td>43,750</td>
<td>7.3</td>
<td>4</td>
<td>94</td>
</tr>
</tbody>
</table>

molecules on the metal surface acting as barrier to the oxygen diffusion process.

Figure 5 presents the impedance spectra in presence of 10^{-3} M of TN_{10}, when the electrode rotation speed is limited to 500 rpm and 1000 rpm after 1 h of immersion time. No marked effect of rotation speed on impedance diagrams is noted. This confirms the appearance of a linear broad field in the cathodic domain, when inhibitor is added, and makes it possible to attribute the first loop to a charge transfer process.

3.3. Film Formed upon Copper Surface

Figure 6(a) presents the sample surface morphology after 24 h of immersion time in 3% NaCl in absence of TN_{10} (reference solution). It can be seen that the copper surface is covered by spongy corrosion products. In contrast, in presence of TN_{10}, Figure 6(b) reveals almost no corrosion products are formed, and the grooves due to the initial surface abrasion remain clearly visible after 24 h immersion. Some precipitates observed are NaCl crystals that appeared because of insufficient surface rinsing to avoid a wash-out of the corrosion products, if they are present at the surface. The comparison of these two figures reveals a marked inhibiting efficiency of TN_{10}.

Figures 7(a) and 7(b) presents the results of EDX analysis; the copper, chloride, and oxygen are detected after the immersion in the reference solution during 24 h. If the electrode is dipped in the solution containing 1 mM TN_{10}, the peak due to the oxygen decreased dramatically. There is much less corrosion product at the electrode surface. In contrast carbon atoms appear in the inhibiting test, which suggests the adsorption of inhibitor to the electrode surface. The impedance spectra exhibit, as presented above, a time constant allocable to a dielectric surface film. It is very likely that there is a formation of complex layer with TN_{10} and the corrosion products but its thickness is too thin for SEM observation.

4. Conclusions

Electrochemical study showed that TN10 product tested
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Figure 7. EDAX spectra obtained at the copper surface after 24 h corrosion in the corrosion test solution (a) In absence and (b) In presence of TN10.

is a good corrosion inhibitor, against copper corrosion in 3% NaCl. The inhibitor acts at the same time on the anodic and cathodic electrochemical processes. Polarisation curves showed that the inhibiting effect of this compound results in a clear decrease of the cathodic and anodic current density values especially in the vicinity of corrosion potential. A remarkable inhibiting effect of TN10 was observed when its concentration is higher than 0.05 mM. Its inhibition effect increases with the increase of inhibitor concentration and reaches 98% at 10⁻³ M. These results were confirmed by impedance tests where it was observed that the effect of inhibitor addition is distinguished by an increase of the charge transfer resistance value and a strong reduction of the electrochemical interface capacity value. Surface exam with SEM has shown that inhibitor addition leads to obtain an electrode area without corrosion products as shown in absence of inhibitor. All these lead to propose formation of strong inhibiting film which could passive the metal with very less passivity current densities value.

REFERENCES


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