Electrochemical and analytical study of corrosion inhibition on carbon steel in HCl medium by 1,12-bis(1,2,4-triazolyl)dodecane

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Abstract

1,12-bis(1,2,4-triazolyl)dodecane (dTC12) is an excellent corrosion inhibitor for carbon steel in deaerated 1 M HCl solution. In this work electrochemical and analytical techniques were used to study the inhibition of corrosion on carbon steel in acidic medium. The carbon steel corrosion inhibition of dTC12 was attributed to the synergistic effect between chloride anion and quaternary ammonium ion. The protective efficiency of the film was higher than 90%, indicating that corrosion of carbon steel in 1 M HCl is reduced by dTC12.

The effect of dissolved oxygen on the inhibition efficiency was also investigated. The results show that the inhibition efficiency increases in early stage and decreases for a long immersion time.

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1. Introduction

Numerous studies on corrosion inhibition using organic compounds have been reported [1–6]. It has been accepted that the corrosion inhibition process results from the formation of organic inhibitor films on the metal surface. The use of surfactants has been less studied [2–5] and it was shown that the inhibition efficiency increases with the number of carbon atoms in the molecule. These compounds have marked inhibition efficiency near their critical micellar concentration (CMC) values. The inhibitor adsorption mode was strictly dependent on the inhibitor structure [2,6]. The inhibitor films can be classified as a chemisorbed film, donating a lone pair of electrons attached to a central adsorption atom in a functional group, as an electrostatic adsorption film and as a precipitation and/or a complex film, reacting with dissolved metal ion and organic inhibitor molecule [6]. Although, it is important to know how organic inhibitor films grown on the metallic surface in order to achieve good corrosion inhibition.

In this paper, the authors present a study on the inhibiting effect of the dTC12 in case carbon steel exposed to aggressive solutions of 1 M HCl. The aim of the present study is to understand and to discuss the mechanism of protection given by this compound. Electrochemical measurements were used to investigate the corrosion inhibition and surface analysis was used to identify the compounds present on the inhibitive layer.

2. Experimental

2.1. Inhibitor

1,12-bis(1,2,4-triazolyl)dodecane (dTC12) was prepared from 1,2,4-triazole and the 1,12-dibromo alkane using the phase transfer catalysis method (PTC) [7]. The product was purified and characterised by elemental analysis, $^1$H NMR, $^{13}$C NMR and mass spectra [8].

2.2. Steel samples

Commercial carbon steel of the following chemical composition other than iron: %C: 0.2; %P: 0.005; %S: 0.05; %N: 0.07 (AFNOR NORM) was used.

2.3. Electrochemical techniques

2.3.1. Polarisation measurements

Electrochemical measurements were conducted in a conventional three-electrode cylindrical glass and thermo stated cell. A platinum disc was used as counter elec-
trode and the Ag/AgCl as reference electrode. The working electrode was a carbon steel disc. The specimens were machined into cylinders and mounted in polytetrafluoroethylene (PTFE) moulds. The area in contact with the corrosive solution was 0.5 cm².

The potentiodynamic polarisation curves were recorded using an EGδG instrument (model M 352A). The working electrode was initially kept at the corrosion potential for 30 min before recording the cathodic curves up to the −750 mV vs. Ag/AgCl using a potential step of 0.5 mV/s.

2.3.2. Impedance measurements

Impedance (EIS) measurements were done by using a EGδG apparatus. The measuring ranged from 100 kHZ down to 10 mHz, using a 5 mV (rms) sinusoidal potential perturbation. Experiments were performed in the potentiostatic mode.

2.3.3. Scanning vibrating electrode technique

The scanning vibrational electrode technique (SVET) measurements were performed using an Applicable Electronics apparatus. The scanned area was 1 × 1 mm².

2.4. Analytical study

2.4.1. X-ray photoelectron spectroscopy

The chemical composition of the surface was determined by X-ray photoelectron spectroscopy (XPS) using a non-monochromated Mg (Kα) photon source. The experiments were performed using a Vg Scientific Microlab 310F equipped with a concentric hemispherical analyser. Spectra were taken in “constant analyser energy mode” (CAE = 30 eV). For these conditions the energy resolution is approximately 0.9 eV.

3. Results and discussion

3.1. Potentiodynamic measurements

Fig. 1 shows the cathodic polarisation curves in deaerated 1 M HCl solutions without and with addition of dTC12 at different concentrations. This figure shows a monotonic evolution of the current with the potential. The current density decreases with increasing inhibitor concentrations and the corrosion potential shifts, depending on the inhibitor concentration.

The values of the electrochemical parameters obtained from the curves depicted in Fig. 1, namely: corrosion potential ($E_{corr}$), cathodic Tafel slope ($bc$), corrosion current density ($I_{corr}$) and inhibition efficiency ($E\%$) for the different concentrations of dTC12 are given in Table 1.

The dTC12 inhibition efficiency in each case was calculated according to Eq. (1).

$$E\% = \left(1 - \frac{I_{corr}}{I'_{corr}}\right) \times 100$$ (1)
where $I_{corr}$ and $I'_{corr}$ are the corrosion current density in the absence and in the presence of dTC12, respectively.

The results depicted in Table 1 show a decrease of the corrosion current density with increasing dTC12 concentrations. At concentration higher than $5 \times 10^{-3}$ M the efficiency seems to approach a constant value. It means that critical micellar concentration has been attained. The CMC value of dTC12 was determined in corrosive solution without the working electrode, being around $6.3 \times 10^{-3}$ M. The decrease of CMC from $6.3 \times 10^{-3}$ M to $5 \times 10^{-3}$ M can be attributed to the effect of Fe$^{2+}$ and/or Fe$^{3+}$ release from anodic activity on the surface of the steel electrode. This phenomenon has been observed elsewhere [9]. Indeed, it was shown that surfactants inhibitors give a maximum inhibiting effect at critical micellar concentration [4]. The addition of dTC12 also leads to a change of cathodic Tafel slopes. This result indicates that inhibitor addition modify the mechanism involved in the cathodic process.

Table 1
Electrochemical parameters from polarisation measurements on carbon steel in 1 M HCl without and with different inhibitor concentrations

<table>
<thead>
<tr>
<th>C_{inhibitor} (mol/l)</th>
<th>$E_{corr}$ (mV/Ag–AgCl)</th>
<th>$I_{corr}$ (µA/cm²)</th>
<th>$bc$ (mV/dec)</th>
<th>$E$%</th>
<th>CMC (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>0</td>
<td>-465</td>
<td>137</td>
<td>88</td>
<td>–</td>
</tr>
<tr>
<td>dTC12</td>
<td>$10^{-5}$ M</td>
<td>-482</td>
<td>61</td>
<td>146</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>$10^{-4}$ M</td>
<td>-487</td>
<td>39</td>
<td>158</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$ M</td>
<td>-472</td>
<td>25</td>
<td>173</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>$5 \times 10^{-3}$ M</td>
<td>-473</td>
<td>15</td>
<td>191</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>$10^{-2}$ M</td>
<td>-472</td>
<td>9</td>
<td>203</td>
<td>93</td>
</tr>
</tbody>
</table>

Fig. 1. Cathodic polarisation curves of steel in 1 M HCl with and without dTC12 at different concentrations.
3.2. Electrochemical impedance spectroscopy

Fig. 2 shows the impedance spectra obtained for the carbon steel electrode in the presence of $10^{-2}$ M dTC12. In the absence of inhibitor only one capacitive loop is observed, however in the presence of inhibitor the spectrum show the presence of two time constants.

In the absence of inhibitor the capacitive loop can be attributed to the charge transfer reactions, occurring on the steel surface. The total impedance of this system is more then one order of magnitude lower than that observed in the presence of inhibitor. This behaviour was expected since the solution is a very aggressive medium. However, in the presence of inhibitor two time constants are observed in the impedance spectrum. The high frequency and low frequency loops observed in presence of dTC12 can be attributed to the formation of an inhibitor film and to the Faradic processes occurring through defects of this film, respectively.

3.3. Determination of the zero charge potential (ZCP)

A surfactant usually acts at the solid surface by forming an adsorption film or by inducting the formation a layer of corrosion products. This adsorption depends on the charge of the metallic surface, the charge or the dipole moment of the inhibitor molecule and the adsorption of other ionic species present on solution [10,11]. The potential of zero charge (ZCP) plays a very important role in the electrostatic adsorption process. To know if the charge of the electrode is positive or negative the difference between the corrosion potential and ZCP of the corroding metal was determined. Thus, a set of impedance spectra for carbon steel in 1 M HCl solutions in a potential range between $-700$ and $-300$ mV vs. Ag/AgCl was obtained. Fig. 3 shows the dependence of the double layer capacitance with potential. The plot

![Fig. 2. Electrochemical impedance spectra of steel in 1 M HCl with and without $10^{-2}$ M of dTC12.](image-url)
presents a minimum at $-560 \text{ mV} \text{ vs. Ag/AgCl}$, which is more negative than the corrosion potential ($-465 \text{ mV} \text{ vs. Ag/AgCl}$). This result suggests that the carbon steel surface is positively charged at the open circuit potential.

Considering only electrostatic attraction effects, it is unlikely that positive quaternary ammonium ions present in the inhibitor molecule will directly adsorb on the steel surface. Thus, the reason why dTC12 can inhibit carbon steel corrosion in 1 M HCl solution seems to be related with synergistic effects, resulting from the specific adsorption of chloride ions at the steel/solution interface. These anions are characterised by strong adsorbability on the steel surface. Thus, it is assumed that chloride ions first adsorb on the steel/solution interface, at the corrosion potential, through electrostatic attraction forces between these anions and the excess of positive charges at the carbon steel surface. This effect leads to a change on the solution side of the interface, which becomes negatively charged. Thus, quaternary ammonium cations are able to adsorb electrostatically on the steel surface previously covered with adsorbed chloride ions. Identical results were reported by Ma et al. [10] in a study of the corrosion inhibition of copper in acidic solution using cetyltrimethylammonium bromide as inhibitor. This author found that for inhibitor concentrations higher than $1 \times 10^{-3} \text{ M}$ the electrostatic attraction dominates the adsorption process.

An adsorption model proposed with basis on literature [10] and on the present results is described schematically in Fig. 4.

3.4. Effect of dissolved oxygen

Fig. 5 shows the impedance spectra in aerated 1 M HCl solutions with and without $10^{-2} \text{ M}$ of dTC12. The impedance spectra show only one capacitive loop. The diameter of the capacitive loop increased from $150 \Omega \text{ cm}^2$ in the absence of dTC12
to 750 \( \Omega \text{ cm}^2 \) in the presence of dTC12. Table 2 summarizes the impedance results obtained in deaerated conditions.

Table 2 shows that the value of the capacity decreases from 106 to 33 \( \mu \text{F/cm}^2 \) and that resistance increases, meaning that inhibitor film becomes thinner but more protective, compared to the behaviour observed in the absence of inhibitor. However, the efficiency of the inhibitor in aerated 1 M HCl solution is smaller than that obtained in the deaerated solution. If there is no oxygen in solution the corrosion processes are strongly hindered and thus higher impedances are measured. However, in the presence of dissolved oxygen the corrosion rate increases.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>( R ) (( \Omega \text{ cm}^2 ))</th>
<th>( C ) (( \mu \text{F/cm}^2 ))</th>
<th>( f ) (Hz)</th>
<th>( E% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>150</td>
<td>106.1</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>( 10^{-2} ) M dTC12</td>
<td>750</td>
<td>33.7</td>
<td>4.5</td>
<td>80</td>
</tr>
</tbody>
</table>
The lipid cell membranes are very permeable to small non-polar molecules like O$_2$ [12]. On the other hand, as proposed in previous works [13,14] O$_2$ is transported by a diffusion mechanism through the cell membranes and the high permeability is caused by the higher solubility of O$_2$ in lipid than in water. Since lipid molecules are surfactants and for the present results obtained with synthesis surfactants molecules the decrease of efficiency in presence of oxygen can be attributed to a permeability caused by dTC12 film to oxygen molecules.

In order to confirm the presence of the Warburg the logarithm of the imaginary part with the logarithm of frequency was plotted—Fig. 6. From this plot a straight line with a slope around $-0.5$ can be observed. This behaviour can, thus be attributed to oxygen diffusion from the bulk solution to the electrode surface through the inhibitor film formed on the steel, including the inhibitor molecules and the corrosion products act as a barrier to the oxygen diffusion process.

3.5. Immersion time

Fig. 7 shows the impedance spectra obtained after different immersion times in aerated 1 M HCl with and without $10^{-2}$ M of dTC12.

The evolution of the characteristic parameters associated with the capacitive loop with time is summarized in Table 3.

The diameter of the capacitive loop increases in size with increasing immersion time, reaching a maximum after 12 h, and then starts to decrease. These results indicate that the adsorption model, arrangement and orientation of dTC12 on the surface of the carbon steel, changes with time. Considering that adsorption is essentially controlled by electrostatic attraction, as the immersion time increases, more chlorides will be adsorbed on the surface helping to the formation of the inhibitor layers.
However as soon as all the active sites become saturated with inhibitor, the development of the inhibitor layer is gradually slowed down. Furthermore, with time it seems the inhibiting effect decreases probably because some defects exist on the film leading to the access of aggressive anions to the steel/inhibitor interface. The formation of this weaker sites can be explained with basis in literature[10], where the decrease of the inhibition efficiency was attributed to the formation of hemimicelles aggregates by the initially deposited inhibitor molecules, reducing the effective area covered by the inhibitor. Fig. 8 depicts the surface of the samples after 12 and 24 h and it is clearly shown that the amount of corrosion products increases from 12 to 24 h.

3.6. SVET measurements

The electrochemical behaviour of steel was investigated by SVET. In the absence of inhibitor, Fig. 9, large activity with H₂ bubbling was observed on the surface immediately after immersion. In the first minutes of immersion in the 1 M HCl solution practically all the steel surface shows activity. The current mapping shows
current gradients between $150$ and $200 \ \mu A/cm^2$. The most intense activity was observed during the first 30 min. After this time the current gradient became more
positive (around $-15 \ \mu A/cm^2$ after 2 h). For longer immersion times the surface appears corroded, less $H_2$ release was observed and the current gradient was about $-50 \ \mu A/cm^2$ after 7 h.

In the absence of inhibitor—Fig. 9, the large negative currents observed suggest the movement of positive charges from the bulk of solution to the steel surface or movement of negative charges from surface to solution. The first situation seems to be more realistic. Thus, the main cathodic reaction in the surface is hydrogen evolution, as expected in acidic medium and visually confirmed by the strong hydrogen activity. Consequently it is expected a migration of $H^+$ from the solution to feed the cathodic sites on the surface. With time, the current gradient becomes more positive, suggesting that the flux of $H^+$ becomes less intense. The reason can be due to the formation of corrosion products, which may cover the surface, decreasing cathodic activity.

Fig. 10 shows the SVET maps during the first stages of immersion in the solution containing inhibitor and no activity was detected on the steel surface. The current maps reveal current gradients of about $+5 \ \mu A/cm^2$, thus suggesting flux of cationic species from the surface to the bulk solution. This may suggest the presence of some anodic activity in order to create favourable sites for inhibitor adsorption on the surface. Thus, this can be related with the formation of the primary chloride rich layer.
over which the inhibitor layer starts to develop, in accordance with the proposed model. Some activity was detected latter, however no significant effects on the measured current were observed. The presence of inhibitor seems to suppress the cathodic reaction and no significant activity was observed during the evolution of the experiment (7 h). Comparatively to the non-treated sample, and for the same immersion times, the currents are positives and close to zero and no H₂ bubbling was. Thus, the presence of inhibitor leads to a strong decrease of corrosion activity, in good agreement with the previous electrochemical results.

3.7. XPS analysis

The chemical composition of the samples was determined by XPS. Fig. 11 depicts the XPS spectrum for N1s ionisation. The spectrum reveals the presence of two partially superimposed peaks: one at approximately 400 eV, which can be assigned to the presence of N–CH bonds present in the inhibitor molecule and another at slightly higher energies (401.7 eV). The presence of this high binding energy shoulder is characteristic of the formation of protonated amino groups on the surface, thus in accordance with the model previously discussed. Previous XPS studies on interactions of aminoalcohols with steel surfaces [15] also report the presence of protonated groups on the steel surface. This study also concludes that the inhibitor is stable and strongly chemisorbed on the surface, even in the presence of chloride ions. This observation agrees with the results obtained in the present work, since good inhibition was observed in the presence of chloride ions.

The results obtained in the present work help to discuss the mechanism of interaction of the inhibitor with the metallic surface and evidences the role of the chloride ions in such process. These ions have a synergistic effect on the deposition process, changing the surface charge and helping to the fixation of the protonated amino groups on the surface. Moreover the present study shows that the inhibitor strongly helps to the reduction of the cathodic activity hindering the cathodic reactions.

Fig. 11. N1s spectrum for the sample treated with inhibitor.
4. Conclusions

The 1,12-bis(1,2,4-triazolyl)dodecane (dTC12) acts as a good cathodic inhibitor of carbon steel in deaerated 1 M HCl solution. The efficiency is of the inhibitor at concentrations of $10^{-2}$ M dTC12 is around 94%.

The carbon steel surface is positively charged in HCl solutions at the open corrosion potential, but becomes negatively charged when chloride ions are present. The adsorption of dTC12 is attributed to the synergistic effect between chlorides anions and positive quaternary ammonium ions present in the inhibitor molecule.

Comparison of the inhibitor efficiency in aerated and deaerated 1 M HCl solution shows that the inhibitor effectiveness decreases in presence of dissolved oxygen. In aerated solution the inhibition efficiency of dTC12 decreases with the immersion time.

The inhibitor acts by stopping hydrogen evolution reactions and decreasing cathodic currents. However, for long immersion times, the inhibitive efficiency decreases.

References

[1] Proceedings of the 1st to 8th European Symposium on Corrosion Inhibitors, every 5 years held in Ferrara.