Research Article

Sodium Citrate as an Environmentally Friendly Corrosion Inhibitor of Steel in a Neutral Environment

Mariia Olena Danyliak,1 Ivan Zin,1,2 Yuliia Rizun,1 and Sergiy Korniy1

1Karpenko Physico-Mechanical Institute of the NAS of Ukraine, Lviv, Ukraine
2Lviv Polytechnic National University, Ukraine

Correspondence should be addressed to Sergiy Korniy; korniy_sergiy@ukr.net

Received 22 September 2022; Revised 1 November 2022; Accepted 2 November 2022; Published 21 November 2022

Academic Editor: Senthil Kumaran Selvaraj

Copyright © 2022 Mariia Olena Danyliak et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this work we investigated the inhibiting effect of sodium citrate, an environmentally safe corrosion inhibitor, on low-alloy steel 09G2S in a neutral environment using electrochemical methods. Potentiodynamic studies showed that sodium citrate reduces corrosion currents of 09G2S steel in a 0.1% NaCl solution and reaches its maximum efficiency at a concentration of 2.5 g/l. Electrochemical impedance spectroscopy results indicate the adsorption of citrate ions and the formation of a protective film, which probably consists of Fe-citrate complexes. The formation of a protective film on the steel surface in sodium citrate-inhibited solutions was confirmed by the results of scanning electron microscopy and EDX analysis. Hence, our research shows that sodium citrate has satisfactory anticorrosion properties and can be used as a basic component during the development of environmentally safe inhibitor compositions for the protection of low-alloyed carbon steels in neutral environments of recirculating water supply systems in petroleum refineries, petrochemical plants, and other industries.

1. Introduction

Corrosion inhibitors are one of the most practical and cost-effective methods of anticorrosion protection. They are widely used to protect metals and alloys from the effects of corrosive environments. Corrosion inhibitors can be organic or inorganic in nature [1–7] and are classified depending on the method of use and the specificity of the inhibitory effect. However, a significant part of them can pose a danger to the environment and people. Therefore, there is a need to minimize the use of such harmful substances and to replace them with environmentally safe alternatives. Great examples of alternative inhibitors are substances based on natural products, e.g., plant extracts [8–13]. In addition to being environmentally friendly, such inhibitors have high solubility and effectiveness. Besides, they are readily available on the market and are cost-efficient, which altogether makes them very attractive for industrial use [14, 15].

Carboxylic acid salts are used as corrosion inhibitors or as components of synergistic anticorrosion compositions, which are environmentally safe and effective against corrosion in a number of metals and alloys in various environments [16–18]. A typical inhibitor for steel, zinc, copper, and aluminum alloys is sodium benzoate (C6H5COONa)—the sodium salt of benzoic acid [19, 20]. Sodium potassium tartrate is an effective cosynergist in inhibiting composition for the protection of aluminum alloys in 0.5% NaCl solution [21]. Furthermore, the inhibition efficiency of sodium potassium tartrate in combination with propargyl alcohol was shown for aluminum alloy AA3003 in a 0.5% NaCl solution [22]. The components of the mixture demonstrated satisfactory efficiency at concentrations of 1–1.5 mm when used separately. But when they were combined, a synergistic effect was observed resulting in overall higher inhibition efficiency. The optimum ratio of tartrate to alcohol in the mixture was 5:2.

Numerous papers report the inhibitory efficiency of the sodium salt of citric acid Na3C6H5O7 [23, 24]. The inhibition of steel corrosion by sodium citrate in an environment simulating a corrosive solution in the pores of concrete, in the presence and absence of chloride anions, was investigated in the work of [25]. 200 ppm sodium citrate was...
shown to provide 98% corrosion inhibition efficiency in the absence of chloride anions. In another work [26], the protective anticorrosion effect of phosphonic acid was enhanced by sodium citrate to inhibit the corrosion of low-carbon steel in a neutral chloride environment. The maximal effectiveness of the corrosion inhibition was achieved at 25 ppm of sodium citrate. Based on these findings, it was hypothesized that corrosion inhibition occurs due to the formation of a protective layer consisting of “Fe²⁺-sodium citrate” complex compounds on the metal surface.

Thus, the research of anticorrosion properties of carboxylic acid salts, both as individual substances and components of inhibitory compositions, is highly relevant for the development of environmentally safe industrial inhibitors.

Low-alloy silicon-manganese steel 09G2S is widely used to manufacture recirculating water supply systems in petrochemical plants, and oil production equipment [27, 28]. The low-carbon content in this steel is combined with a ferrite/lamellar pearlite structure. Until now, the effect of citrates on the corrosion of silicon-manganese steels has not been sufficiently studied.

Therefore, the purpose of this work is to investigate the inhibitory effect of sodium citrate (sodium salt of citric acid) to increase the corrosion resistance of low-alloy structural steel 09G2S in neutral environments.

2. Materials and Methods

Sodium citrate (\(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\)) in the form of a white crystalline powder was added to the corrosive medium. The sodium salt of citric acid is a water-soluble environmentally safe substance; citric acid is a part of the metabolic cycle of living organisms. It is widely used in the food industry mainly as a flavour additive or preservative. Its structural formula is depicted in Figure 1.

In this study, samples of the low-alloy low-carbon steel 09G2S were used. The steel composition is provided in Table 1.

2.1. Potentiodynamic Studies. The corrosion resistance of 09G2S steel was investigated by the method of potentiodynamic polarization in a 0.1% NaCl solution with the addition of sodium citrate at different concentrations (0.5–3.0 g/l), using an MTech COR-500 potentiostat, an Ag/AgCl reference electrode, and an auxiliary platinum electrode. The potential scanning rate during the experiments was 2 mV/s.

The working area of the steel sample was 1 cm². The polarization curves of 09G2S steel after 3 and 24 h of exposure to a 0.1% NaCl solution with different concentrations of sodium citrate were recorded.

2.2. Electrochemical Impedance Spectroscopy. The corrosion resistance of 09G2S steel was also investigated by the method of electrochemical impedance spectroscopy (EIS). For this, a three-electrode cell was used, which consisted of a saturated silver/silver chloride reference electrode, a platinum auxiliary electrode, and a working electrode—the test sample. Impedance measurements were carried out at open circuit potential using a VersaSTAT 3 potentiostat-frequency response analyzer in the frequency range of 10000–0.01 Hz. The amplitude of the applied signal was 10 mV. An equivalent electrical circuit, which included solution resistance \(R_s\), charge transfer resistance \(R_{ct}\), double layer capacitance as constant phase element (CPE), was used to calculate the components of the impedance (Figure 2).

2.3. Scanning Electron Microscopy. The surface morphology and elemental composition of the 09G2S steel upon exposure to the studied solutions were investigated on a Zeiss EVO-40XVP scanning electron microscope (SEM) with an INCA Energy 350 EDS X-ray microanalysis system. A Zeiss Stemi 2000-C optical metallographic microscope with a Sigeta video camera and appropriate image processing software was used to study the microtopography of the surface of the samples.

2.4. Gravimetric Studies. Gravimetric tests were performed on 09G2S steel samples of rectangular shape 20 × 15 mm in size and 2.5 mm thick. Before the test, the surface of the samples was cleaned and polished on grinding wheels with fine abrasive paper. The samples were degreased with acetone, dried, and kept in a desiccator for 2 h. After exposure to the corrosive solution, the samples were dried, mechanically cleaned from corrosion products with a white eraser, washed in acetone, dried again, and weighed.

The corrosion rate \(K_m\) (g/cm²·h) was determined after sample exposure to corrosion solution. The calculation was done according to the formula:

\[
K_m = \frac{\Delta m}{S \tau},
\]

where \(\Delta m\) is the change in sample weight after exposure to a corrosive environment and removal of corrosion products, g; \(S\) is the sample area, cm²; and \(\tau\) is its exposure time, h.

The degree of protection in the environment with sodium citrate was determined according to the following formula:

\[
Z = \frac{K_{\text{uninh}} - K_{\text{inh}}}{K_{\text{uninh}}} \times 100\%,
\]

where \(K_{\text{uninh}}, K_{\text{inh}}\) is the steel corrosion rate in uninhibited and inhibited environments, respectively.

3. Results and Discussion

The polarization curves of 09G2S steel after 3 and 24 h of exposure to a 0.1% NaCl solution with different concentrations of sodium citrate are shown in Figure 3. The corrosion potential \(E_{\text{cor}}\) and density of corrosion current \(I_{\text{cor}}\) were determined from the polarization data. After 3 h of exposure,
the electrochemical characteristics of steel indicate an increase in its corrosion resistance in inhibited solutions, as evidenced by a decrease in corrosion currents. The maximum protective effect is observed at an inhibitor concentration of 2.5 g/l and it persists for 24 h, probably due to the adsorption of citrate ions on the steel surface. The subsequent increase in concentration to 3.0 g/l does not result in further increase of the inhibitory effect of sodium citrate (Table 2). The polarization dependencies show that the citrate inhibitor slows down the metal oxidation and oxygen reduction reactions that occur at the anode and cathode, respectively. In the presence of sodium citrate in the

![Figure 2: The equivalent electrical circuit for fitting EIS spectra.](image)

![Figure 3: Polarization curves of 09G2S steel after 3 hours (a) and 24 hours (b) of exposure to a 0.1% NaCl solution with sodium citrate concentration of (1) 0 g/l, (2) 0.5 g/l, (3) 1.0 g/l, (4) 1.5 g/l, (5) 2.0 g/l, (6) 2.5 g/l, and (7) 3.0 g/l.](image)

**Table 1: Chemical composition of steel 09G2S.**

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel 09G2S</td>
<td>≤0.12</td>
<td>0.5-0.8</td>
<td>1.3-1.7</td>
<td>≤0.3</td>
<td>≤0.25</td>
<td>≤0.3</td>
<td>≤0.04</td>
<td>≤0.03</td>
<td>Balance</td>
</tr>
</tbody>
</table>

**Table 2: Electrochemical characteristics of steel 09G2S after exposure to 0.1% NaCl solution with different concentrations of sodium citrate.**

<table>
<thead>
<tr>
<th>C (g/l)</th>
<th>$E_{cor}$ (V)</th>
<th>3 hours $i_{cor}$ (mA/cm²)</th>
<th>Exposure time</th>
<th>24 hours $i_{cor}$ (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.55</td>
<td>$7.0 \times 10^{-3}$</td>
<td></td>
<td>$-0.67$</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.51</td>
<td>$6.8 \times 10^{-3}$</td>
<td></td>
<td>$-0.64$</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.53</td>
<td>$6.4 \times 10^{-3}$</td>
<td></td>
<td>$-0.63$</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.43</td>
<td>$4.5 \times 10^{-3}$</td>
<td></td>
<td>$-0.65$</td>
</tr>
<tr>
<td>2</td>
<td>-0.43</td>
<td>$4.0 \times 10^{-3}$</td>
<td></td>
<td>$-0.62$</td>
</tr>
<tr>
<td>2.5</td>
<td>-0.50</td>
<td>$3.4 \times 10^{-3}$</td>
<td></td>
<td>$-0.56$</td>
</tr>
<tr>
<td>3.0</td>
<td>-0.53</td>
<td>$5.6 \times 10^{-3}$</td>
<td></td>
<td>$-0.66$</td>
</tr>
</tbody>
</table>

International Journal of Corrosion
corrosive environment, the cathodic and anodic currents of steel decrease approximately equally, and the shift in the corrosion potential is insignificant, which indicates mixed control of metal corrosion by this inhibitor. The inhibitor protective effect can probably be associated with the formation of an adsorption monolayer of citrate ions with complete saturation of the adsorption bonds on the surface.

Samples of 09G2S steel were investigated upon exposure to solutions with different sodium citrate content using the method of electrochemical impedance spectroscopy (EIS). It should be noted that the results of polarization measurements are consistent with EIS studies.

It was discovered that the value of the charge transfer resistance of the steel sample increases with increasing content of sodium citrate in the solution, and at a concentration of 2.5 g/l, the resistance value is 3 times higher compared to an uninhibited solution of 0.1% NaCl (Figure 4, Table 3). This result can be attributed to the adsorption of sodium citrate ions with complete saturation of the adsorption bonds on the surface.
citrate on the steel surface due to its hydroxyl and carboxyl functional groups. The introduction of sodium citrate as a corrosion inhibitor into the corrosive solution contributes to the decrease of the CPE, which corresponds to the double-layer capacitance of steel. The parameter $n$ of CPE characterizes the degree of geometric and energy heterogeneity of the metal surface [29]. A decrease in the value of $n$ due to an increase in the duration of exposure to 24 h...

**Figure 6:** The surface of 09G2S steel samples after 24 hours of exposure to a 0.1% NaCl solution inhibited by sodium citrate with a concentration of (a) 0.5 g/l, (b) 1.0 g/l, (c) 1.5 g/l, (d) 2.0 g/l, and (e) 2.5 g/l.
Table 4: Chemical composition (in mass%) of the 09G2S surface after 24 hours of exposure to a 0.1% NaCl solution with different concentrations of sodium citrate.

<table>
<thead>
<tr>
<th>C (g/l)</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Si</th>
<th>Mn</th>
<th>Fe</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8.95</td>
<td>21.61</td>
<td>5.51</td>
<td>0.38</td>
<td>0.85</td>
<td>60.36</td>
<td>2.34</td>
</tr>
<tr>
<td>1.0</td>
<td>8.11</td>
<td>22.74</td>
<td>—</td>
<td>0.79</td>
<td>1.72</td>
<td>64.80</td>
<td>1.84</td>
</tr>
<tr>
<td>1.5</td>
<td>7.74</td>
<td>9.98</td>
<td>—</td>
<td>0.44</td>
<td>0.95</td>
<td>73.20</td>
<td>1.13</td>
</tr>
<tr>
<td>2.0</td>
<td>2.65</td>
<td>2.52</td>
<td>0.86</td>
<td>0.74</td>
<td>1.00</td>
<td>92.06</td>
<td>0.17</td>
</tr>
<tr>
<td>2.5</td>
<td>3.30</td>
<td>3.04</td>
<td>1.28</td>
<td>0.56</td>
<td>1.16</td>
<td>90.36</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table 5: Corrosion rate ($K_m$, g/cm²·h) and degree of protection (Z, %) of 09G2S steel in 0.1% NaCl solution.

<table>
<thead>
<tr>
<th>Environment</th>
<th>$K_m$</th>
<th>Z</th>
<th>$K_m$</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% NaCl solution</td>
<td>2.14 · 10⁻⁵</td>
<td></td>
<td>1.48 · 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>0.1% NaCl solution + 2.0 g/l Na₃C₆H₅O₇</td>
<td>8.84 · 10⁻⁶</td>
<td>58.7</td>
<td>7.57 · 10⁻⁶</td>
<td>48.9</td>
</tr>
<tr>
<td>0.1% NaCl solution + 2.5 g/l Na₃C₆H₅O₇</td>
<td>7.33 · 10⁻⁶</td>
<td>65.7</td>
<td>7.52 · 10⁻⁶</td>
<td>49.2</td>
</tr>
</tbody>
</table>

indicates a change in surface heterogeneity, which can probably be associated with the formation of both a protective film and a partial accumulation of corrosion products on the steel surface (Table 3).

An increase in the maximum of frequency dependence of the steel phase angle and its shift towards higher frequencies of alternating current in the inhibited corrosive solution also indicate the formation of a protective film with improved barrier properties on the electrode surface (Figure 5).

After 24 h of exposure to a 0.1% NaCl solution with the addition of sodium citrate, the surface of the 09G2S steel was examined by scanning electron microscopy, and its chemical composition was determined using EDX analysis (Figure 6, Table 4). Upon exposure to the environment inhibited by sodium citrate with a concentration of 0.5 g/l, the surface of 09G2S steel is developed and covered with corrosion products, namely, iron oxides/hydroxides. Also, Cl⁻ content was found on the surface of the studied material, which is obviously related to the formation of iron chlorides on steel after 24 hours of exposure according to the reaction: Fe^{2+} + 2Cl⁻ → FeCl₂ [30]. It was previously shown that corrosion products of steel in a chloride-containing environment may contain akaganite FeO(OH,Cl) [31, 32]. Also iron hydroxychloride b-Fe₆(OH)₃Cl can be present in corrosion layers on steel [33]. In addition, it should be noted that the Na content on the metal surface is probably related to the accumulation of sodium chloride in corrosion products.

The number of corrosion damages and corrosion products gradually decreases on the steel surface with an increasing concentration of sodium citrate in the corrosive solution (Figure 6). At a sodium citrate concentration of 2.5 g/l, a homogeneous protective film is observed, which blocks the penetration of the corrosive solution to the metal surface. The increased carbon content on the steel surface at low concentrations of sodium citrate (Table 4) is probably related to the adsorption of the inhibitor on a relatively thick layer of corrosion products. At concentrations of 2 g/l and 2.5 g/l of sodium citrate in a corrosive environment, the amount of carbon on the metal surface decreases to 2.65 and 3.3 mass%, respectively, and the Fe content increases to over 90 mass%. At an inhibitor content level of 2.5 g/l, a dense adsorption film (Figure 6(e)) with high protective properties is formed on the steel surface. At the same time, metal corrosion is practically not observed anymore.

The protective film on steel detected by electron microscopy (Figure 6, Table 4) is formed in an inhibited corrosive solution in two ways [34]: (1) acid residues of citric acid are adsorbed on the natural oxide film of steel due to the presence of carboxyl functional groups (−COOH), enhancing its protective effect; (2) they form sparingly soluble complexes with iron cations that cover pores and defects in this film, slowing down the anodic process. The formation of Fe-citrate complexes can occur according to the following reactions [35]:

\[
\begin{align*}
    Na_3C_6H_5O_7 &\leftrightarrow C_6H_5O_7(ads)^{3−} + 3Na^+ \\
    C_6H_5O_7(ads)^{3−} &\leftrightarrow C_6H_5O_7(ads)^{3−} \\
    Fe^{2+} + C_6H_5O_7(ads)^{3−} &\leftrightarrow [Fe_2(C_6H_5O_7)_2]_{(ads)}^{-} \\
    Fe^{2+} + [Fe_2(C_6H_5O_7)_2]_{(ads)}^{-} &\leftrightarrow [Fe_3(C_6H_5O_7)_2]_{(ads)}^{-}
\end{align*}
\]

The corrosion resistance of 09G2S steel in a 0.1% NaCl solution with the addition of sodium citrate as a corrosion inhibitor was also assessed by the gravimetric method (Table 5). Gravimetric studies were carried out at concentrations of 2 and 2.5 g/l; because in electrochemical studies, sodium citrate showed the highest anticorrosion effect at these concentrations. After 6 h of exposure, the corrosion rate $K_m$ was 1.04 · 10⁻⁴ g/cm²·h in an uninhibited 0.1%
NaCl solution, and no mass loss was detected when adding 2 and 2.5 g/l sodium citrate. When the exposure was increased to 24 h, the degree of steel protection by sodium citrate reached 65.7%, which indicates the satisfactory effectiveness of the selected inhibitor as a possible component of the inhibitory composition.

In the future, the search for synergistic compounds to enhance the protective effect of sodium citrate is needed. The use of 10-methylacridinium iodide for this purpose is already known in the literature [36]. After 96 hours of corrosion tests in an uninhibited environment, the corrosion rate slows down somewhat, which is apparently due to the shielding of the metal surface by corrosion products. On the other hand, the rate of steel corrosion in 0.1% NaCl solution with 2.5 g/l sodium citrate after 96 hours of exposure is reduced by ~2 times, which indicates the essential inhibiting effect of the sodium salt of citric acid.

Analysis of the surface of 09G2S steel based on the results of optical microscopy (Figure 7) after 24 hours of exposure to a sodium chloride solution inhibited by sodium citrate at concentrations of 2 and 2.5 g/l revealed that the samples retained a light grey colour with a characteristic metallic luster, unlike the control sample, the surface of which contained corrosion products and was affected by uneven corrosion.

4. Conclusions

We found that sodium citrate inhibits the corrosion of low-alloy steel 09G2S in a 0.1% NaCl solution. Its maximum effectiveness is observed at a concentration of 2.5 g/l. Due to the presence of carboxyl functional groups, citrate ions are adsorbed on the natural oxide film of steel, enhancing its protective effect, and form sparingly soluble complexes with iron cations that cover pores and defects in this film, slowing down the anodic process. Hence, sodium citrate has satisfactory anticorrosion properties and can be used as a basic component during the development of environmentally safe inhibitor compositions for the protection of low-alloyed carbon steels in neutral environments of recirculating water supply systems in petroleum refineries, petrochemical plants, and in other industries.
Data Availability
The data used to support the findings of this study are included within the article.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

Acknowledgments
The work was performed within the research project of young scientists № 06/03-2021 "Development of New Inhibitory Environmentally Friendly Compositions Based on Saccharides and Organic Salts" of the National Academy of Sciences of Ukraine.

References


