Evaluation of the inhibitory effect of some derivatives of salts of long-chain carboxylic acids in relation to pitting corrosion of reinforcing steel in concrete


Voronezh State University, 1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract
Derivatives of salts of long chain carboxylic acids and dimethylaminopropylamine, including those similar in composition to vegetable oils were synthesized. The structure of the molecules of new substances was reliably confirmed using physical methods of IR-Fourier spectroscopy, NMR spectroscopy, and HPLC.

The inhibitory effect of the synthesized substances on 35GS grade reinforcing steel was assessed using voltammetry. Experiments were carried out in an aqueous extract from a mortar, simulating the concrete pore solution, in the presence of chlorides as activators of pitting corrosion, as well as in samples of fine-grained concrete with periodic immersion in a chloride solution. It was found that 3-(dimethylamino)propyl-1-ammonium stearate did not exhibit an inhibitory effect. The introduction of salts of fatty acids of coconut and sunflower oils increased the anti-corrosion properties. The degree of protection was 40-44% in aqueous solutions and 30-32% for concrete samples.

The time before the onset of corrosion in concrete samples was found to increase by 1.75 times compared to the control composition without additives.

Keywords: Reinforcing steel, Reinforced concrete, Corrosion inhibitors, Chlorides, Long-chain salts carboxylic acids

Funding: The study was supported by the Russian Science Foundation (RSF), project no. 22-23-01144, https://rscf.ru/en/project/22-23-01144/


The content is available under Creative Commons Attribution 4.0 License.
1. Introduction

Reinforced concrete is widely used in the construction of industrial and civil facilities (transport structures, nuclear power plant cooling towers, dams, piers, etc.). The corrosion of reinforcing steel is the main cause of failure of reinforced concrete structures [1]. The most common and dangerous form of corrosion from an operational point of view is caused by the action of chlorides [2], which are contained in large quantities in sea water and de-icing salts. The danger is due to the local nature of steel degradation (pitting, ulcers), which in a relatively short period of time can lead to the destruction of the structure, since it is very difficult to identify local damage using traditional monitoring methods (for example, during visual inspection).

Measures for the primary protection of reinforced concrete against corrosion at the manufacturing stage include the selection of its optimal composition [3], and inhibitor additives are often used to increase the corrosion resistance of reinforcing steel [4]. At the same time, the issue of environmental load during their use remains relevant. The negative impact of nitrites, chromates, and benzotriazole on the environment was repeatedly mentioned [5, 6], despite their rather high protective properties [7–10]. To solve this problem, so-called “green” corrosion inhibitors are proposed for use [11]. Mainly these inhibitors are extracts of products of plant origin: leaves and stems [12–14], fruits [15], and waste products [16, 17]. It is understood that the components contained in the extract are of natural origin and decompose when released into the environment without causing harm. The results presented in published studies convincingly prove the promise of using some extracts as inhibitors in acidic, neutral, and alkaline environments, which provide a degree of protection of more than 80–90%.

A development of this approach in the search for new corrosion inhibitors is the modification of large-scale production products (vegetable oils: sunflower, coconut; food and industrial waste, etc.) using one-stage organic synthesis [18]. At the same time, the issue of rational waste disposal is solved (or cost reduction from the use of inexpensive components) and an increase in protective properties, solubility, or other characteristics is achieved through the introduction of appropriate functional groups. There are examples of modification of soybean, palm, and castor oils with imidazolines [19] with protection levels of low-carbon steel in 1 M HCl of more than 80%. At the same time, a more significant protective effect was noted relative to derivatives based on individual carboxylic acids with the C12, C18 length of the alkyl radical (degree of protection from 60%). In [20], derivatives of maize, soybean, sunflower oils, and beef fat with di- and triethanolamine were studied for steel in an acidic medium simulating the conditions of drilling fluid during oil production. In most combinations studied, protective effects of up to 40–50% were obtained (for several combinations up to 80%). Examples of results with different inhibitory effects allow researchers to take into account existing experience and accordingly select methods for modifying natural compounds and corrosion test conditions to obtain the greatest degree of protection.

There are known examples of the effective action of short-chain carboxylic acids and their salts for the protection of reinforcing steel from corrosion caused by chlorides. In [21], the degree of protection for sodium succinate was established at the level of 55–77% in a model aqueous solution at a chloride concentration of 0.6 M. The authors of [22] showed a decrease in the effectiveness of the protective action in the series of salts malonate > formate > acetate > propionate in samples of fine-grained concrete. In [23] an increase in the protective properties of concrete with the addition of long-chain carboxylic acids during freeze/thaw cycles in the presence of chlorides was revealed. However, there is no mention of the use of modified long-chain carboxylic acids or vegetable oils in solving similar problems.

The purpose of the study was the synthesis and evaluation of the inhibitory effect of new derivatives of salts of long-chain carboxylic acids and dimethylaminopropylamine, including those similar in composition to vegetable oils, in relation to low-carbon reinforcing steel in an aqueous chloride solution simulating the concrete environment, as well as for fine-grained concrete samples during periodic immersion in a chloride solution.
2. Experimental

2.1. Synthesis and analysis of dimethylaminopropylamine derivatives

Ammonium salts of dimethylamino-propylamine with stearic acid and mixtures of fatty acids simulating the composition of vegetable oils (coconut and sunflower) were obtained as inhibitors of chloride corrosion of reinforced concrete (Table 1). The choice of mixtures was determined by the need to assess the possibility of using plant raw materials to obtain inhibitors of this class. All reagents used were purchased from Acros Organics.

High-performance liquid chromatography with high-resolution mass spectrometry (electrospray ionization, HPLC-HRMS-ESI) in combination with UV detection was used to analyse the resulting substances. The analyser unit included an Agilent 1269 Infinity chromatograph and an Agilent 6230 TOF LC/MS detector. Quantitative analysis was performed using an external standard method. 1H NMR spectra were recorded using a Bruker AV600 (600, 13 MHz) spectrometer in a DMSO-d6. TMS was used as the internal standard. The IR spectrum was recorded on Vertex 70 FT-IR spectrometer using a Platinum ATR (Bruker) ATR attachment equipped with a diamond prism in the frequency range from 4000 to 400 cm⁻¹ with a resolution of 2 cm⁻¹. The result was obtained by averaging 16 scans.

The study demonstrated that in the absence of a catalyst, when equimolar amounts of dimethylaminopropylamine and carboxylic acids (or mixtures) are boiled in ethanol, a neutralization reaction takes place with almost quantitative yields of the corresponding ammonium salts, this was confirmed by the data of LC/MS spectrometry, 1H NMR-, IR spectroscopy.

A mixture of 1 mol of acid (in the case of mixtures, the total amount of substance of all acids should be 1 mol) and 1 mol of amine in 50 ml of ethyl alcohol was boiled until the components were completely dissolved. The completeness of the reaction was monitored using a universal indicator and TLC. After completion of the neutralization process, the resulting homogeneous solution was evaporated from the solvent using a rotary evaporator.

3-(dimethylamino)propyl-1-ammonium stearate A. The yield was 96%, viscous amber paste. 1H NMR (δ): 0.89–0.93 (t, 3H CH₃), 1.17–1.91 (m, 34H 15CH₂+CH₂), 2.23–2.30 (s, 6H 2CH₃), 2.61–2.67 (m, 2H CH₂). IR spectrum (cm⁻¹): 3300–3400 (OH+N+-H), 1457, 1375, 1231 cm⁻¹ (O-C≡N). Table 1. Studied inhibitors

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3-(dimethylamino)propyl-1-ammonium stearate</td>
<td>C₁₇H₃₅N⁺O⁻H₂N⁺</td>
</tr>
<tr>
<td>B</td>
<td>3-(dimethylamino)propyl-1-ammonium salts of coconut fatty acids</td>
<td>R: (A)C₁₀H₁₈ (10%) : C₁₇H₃₅ (10%) : C₁₉H₄₁ (50%) : C₁₇H₃₇ (20%) : C₁₇H₃₃ (10%)</td>
</tr>
<tr>
<td>C</td>
<td>3-(dimethylamino)propyl-1-ammonium salts of sunflower fatty acids</td>
<td>R: C₁₇H₃₅ (10%) : C₁₉H₃₇ (40%) : C₁₇H₃₃ (50%)</td>
</tr>
</tbody>
</table>
2150–2200 (N–H), 1700–1750 (C=O), 1550–1600 (COO− + COH), 1500 (N–H), 1400 (N–H), 900–1150 (CH2), 750–800 (CH2), 500–580 (CH3), m/z (M+H): found 386.2841, calculated 386.3872.

1-aminomethyl salts of coconut oil fatty acids

B. The yield was 94%, viscous amber liquid. 1H NMR (δ): 0.89–0.95 (t, 3H CH3), 1.17–1.91 (m, 54H 15CH2+8CH2+CH3), 2.23–2.30 (s, 6H 2CH3), 2.61–2.67 (m, 2H CH2), 2.91–2.95 (m, 2H CH2).

1-aminomethyl salts of fatty acids of sunflower oil C. The yield was 85%, viscous amber liquid. 1H NMR (δ): 0.89–0.95 (t, 3H CH3), 1.17–1.91 (m, 54H 15CH2+8CH2+CH3), 2.25–2.30 (s, 6H 2CH3), 2.61–2.67 (m, 2H CH2), 2.91–2.95 (m, 2H CH2).

2.3. Assessment of the corrosion inhibition properties

To evaluate the corrosion inhibition properties of the synthesised compounds, a set of electrochemical methods was used. Samples of low-carbon steel 35GS with a rectangular cross-section were used as a working electrode. All surfaces, with the exception of the working surface, were reinforced with epoxy resin. A saturated silver chloride reference electrode (SCE, potential +201 mV relative to a standard hydrogen electrode) was placed in a separate container connected to the electrolytic cell by a saturated potassium nitrate solution. The potentials in the work are presented relative to the SCE. The auxiliary electrode was a platinum mesh.

The working solution was a water extract from cement powder (mass ratio of distilled water and cement powder 1:10, extraction for 24 hours followed by filtration, pH 12.5–15.0). Electrochemical measurements were conducted in a glass three-electrode cell with undivided electrode spaces at a temperature of 23±3°C under natural aeration conditions, in the presence of the activating additive of NaCl with the concentration of 1.00 mol·dm−3 (reference experiment), and the studied substances. Due to their long-chain alkyl components, they are characterised by their low solubility in aqueous solutions. In this regard, their effect was studied at the highest concentration, which for all substances was 0.1 g·dm−3.

The working electrode was preliminarily cleaned with K2000 sandpaper, washed with distilled water, and degreased with chemically pure isopropyl alcohol. The current density i was calculated by dividing the actual current I by the geometric area of the working electrode (2.25 cm²).

For experiments in concrete, pieces of low-carbon steel 35GS of a periodic profile with a length of ≈100 mm and a diameter of 6 mm were used. A copper-insulated current conductor was soldered to one end of the rod. The place of soldering was covered with epoxy resin. The surface of the electrodes was cleaned with P1000 sandpaper (abrasive Al2O3 with a particle size of 14–20 microns) to degree St3 according to ISO 8501-1:2014 and degreased with ethyl alcohol (96%).

A mortar based on a cement-sand mixture was prepared from cement grade M500 according to GOST 10178-85. The water-cement ratio (w/c) was 0.50; the mass ratio of cement and sand was 1:3. Prism samples measuring 160×40×40 mm were formed with the electrode located along the axis. Extraction from the formwork was carried out after 7 days. The samples were cured for 28 days at 100% humidity. Additives of the synthesized substances were introduced together with the mixing water in an amount (relative to the weights of water) similar to the experiments in aqueous solutions.

During the experiment, solution samples were immersed in a 3% NaCl aqueous solution for one day. They were then transferred to a laboratory atmosphere with a natural relative humidity of 55±5% and a temperature of 22±2°C, where they were dried for six days. Afterwards, the cycle was repeated.

The corrosion current density (i cor) was determined by the polarization resistance (PR) method according to F. Mansfeld [24]. After the free corrosion potential (E cor) became stable for 30 minutes, the polarization curve was registered using an IPC-Pro potentiostat in the potentiodynamic polarization mode (potential scan rate of 0.2 mV·s−1) in the range from E cor −30 mV to E cor +30 mV.

The ability of the studied substances to inhibit corrosion was assessed based on the degree of protection calculated using the formula:

$$Z_i = \frac{i_{cor,0} - i_{cor,inh}}{i_{cor,0}} \times 100\%,$$

where $i_{cor,0}$ and $i_{cor,inh}$ are the corrosion current densities in the control experiment and in the presence of an inhibitor, respectively.
For concrete samples, as efficiency criteria, an increase in the number of cycles until the loss of the passive state relative to control samples without additives and the degree of protection ($Z_Q$) based on an estimate of the electric charge $Q$ were considered. The value of $Q$ was determined as the area of a curvilinear trapezoid for a function of the corrosion current density at the time of the experiment. The value of $Z_Q$ was determined using the formula:

$$Z_Q = \left(1 - \frac{Q_{\text{inh}}}{Q_{\text{inh}}} \right) \cdot 100\%,$$

where $Q_{\text{inh}}$ and $Q_{\text{inh}}$ are the electric charges in the control experiment and in the presence of the inhibitor, respectively.

### Table 2. Kinetic parameters of mild steel electrode in water extract from cement + 1.00 mol dm$^{-3}$ NaCl in the presence of derivatives

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$C_{\text{inh}}, \text{g dm}^{-3}$</th>
<th>$E_{\text{cor}}, \text{mV}$</th>
<th>$R_p, \text{k}\Omega\cdot\text{cm}^2$</th>
<th>$b_0, \text{mV}$</th>
<th>$b_1, \text{mV}$</th>
<th>$B, \text{mV}$</th>
<th>$i_{\text{corr}}, \mu\text{A}\cdot\text{cm}^{-2}$</th>
<th>$Z_i, %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>–</td>
<td>–451</td>
<td>9.21</td>
<td>64.3</td>
<td>65.0</td>
<td>31.8</td>
<td>3.44±0.36</td>
<td>–</td>
</tr>
<tr>
<td>A</td>
<td>0.1</td>
<td>–442</td>
<td>7.80</td>
<td>55.8</td>
<td>43.5</td>
<td>24.0</td>
<td>3.02±0.16</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>0.1</td>
<td>–416</td>
<td>10.75</td>
<td>58.6</td>
<td>35.2</td>
<td>22.0</td>
<td>2.06±0.15</td>
<td>40</td>
</tr>
<tr>
<td>C</td>
<td>0.1</td>
<td>–436</td>
<td>11.13</td>
<td>58.2</td>
<td>53.9</td>
<td>21.0</td>
<td>1.93±0.25</td>
<td>44</td>
</tr>
</tbody>
</table>

3. Results and discussion

#### 3.1. Potentiodynamic measurements in water extract from concrete

The introduction of all studied substances, by 11–35 mV, slightly shifted $E_{\text{cor}}$ towards positive values (Table 2), which indicates the predominant effect on the anodic partial reaction of metal oxidation [25]. This was also confirmed by comparing the initial segments of the polarization curves (PC). The cathodic sections of PC for all compounds coincide with the control experiment without an additive (Fig. 1). For compound A the anodic sections of the PC were close (Fig. 1a), with the same polarization, the reduction in current density was not higher than 5%. The addition of
compounds B and C caused a decrease in current density in the anodic sections of the PC by 25% and 38%, respectively (Fig. 1b, c).

The results of calculations of electrochemical parameters using the polarization resistance method are presented in Table 2 and are consistent with the data from the analysis of polarization curves. The value of $Z_i$ at 12% was obtained for the compound A. For mixed additives B and C the degree of protection was higher and amounted to 40 and 44%, respectively.

Taking into account the obtained preliminary results in model solutions, samples of fine-grained concrete (hereinafter referred to as concrete) were made for the most effective compounds B and C.

3.2. Potentiodynamic measurements in fine-grained concrete samples

For concrete samples without additives, a violation of the passive state was obtained in a moisture-saturated and dry state after four immersion cycles during the fifth cycle (Figs. 2a, b, curves 1). This was accompanied by reaching or exceeding a threshold value $i_{\text{cor}} = 0.1 \, \mu\text{A}\cdot\text{cm}^{-2}$ [26]. The introduction of the studied additives in an amount of 0.1 g dm$^{-3}$ relative to the amount of mixing water increased the number of cycles of immersion in the chloride solution. For compounds B and C activation was revealed between the seventh and eighth immersion for the saturated state and the eighth and ninth for the air-dry state (Figs. 2a, b, curves 2). Thus, the introduction of the studied additives increased the period before the onset of corrosion by 1.75 times.

Further modification of the calculated values of $i_{\text{cor}}$ also indicated the manifestation of an inhibitory effect. In general, $i_{\text{cor}}$ for concrete with additives did not exceed the values for control samples.

The calculations of the electric charge are presented in Table 3. After 100 days of experiment after 15 cycles of immersion in chloride solution, the degree of protection for additives B and C were close and amounted to 31 and 32%, respectively.

Table 3. Estimation of the electric charge value according to the corrosion rate data

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$Q$, C·cm$^{-2}$</th>
<th>$Z_i, %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>2.16±0.16</td>
<td>–</td>
</tr>
<tr>
<td>B</td>
<td>1.50±0.12</td>
<td>30.6</td>
</tr>
<tr>
<td>C</td>
<td>1.47±0.13</td>
<td>31.9</td>
</tr>
</tbody>
</table>

Conclusions

In our study, we synthesised and confirmed the structure of derivatives of salts of long-chain carboxylic acids and dimethylaminopropylamine, including those similar in composition to vegetable oils.

Electrochemical methods were used to assess the ability of the synthesised compounds to inhibit corrosion of reinforcement steel in a...
solution simulating concrete pore solution in the presence of chlorides. It has been shown that 3-(dimethylamino)propyl-1-ammonium stearate exhibits virtually no inhibitory effect.

For fatty acid salts of coconut and sunflower oils, the degrees of protection were close and comprised 40 and 44% in aqueous solution and 30 and 31% in concrete, respectively, which characterises the resulting substances as moderately effective inhibitors. At the same time, for concrete samples, an increase in the time before the onset of corrosion by 1.75 times was obtained relative to the control composition without additives.

**Author contributions**

All authors made an equivalent contribution to the publication.

**Conflict of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

**References**


14. Harb M. B., Abubshait S., Etteyeb N., Kamoun M., Dhoubi A. Olive leaf extract as a green corrosion inhibitor of reinforced concrete contaminated with...
Evaluation of the inhibitory effect of some derivatives of salts...


Information about the authors

Oleg A. Kozaderov, Dr. Sci. (Chem.), Docent, Head of the Department of Physical Chemistry, Voronezh State University (Voronezh, Russian Federation).
https://orcid.org/0000-0002-0249-9517
ok@chem.vsu.ru

Dmitry S. Shevtsov, Researcher of the Department of Physical Chemistry, Voronezh State University (Voronezh, Russian Federation).
https://orcid.org/0000-0005-4480-787X
shevtsov@chem.vsu.ru

Mikhail A. Potapov, Researcher of the Department of Physical Chemistry, Voronezh State University (Voronezh, Russian Federation).
https://orcid.org/0000-0002-1795-7605
amidines@mail.ru

Iliya D., Zartsyn, Dr. Sci. (Chem.), Professor of the Department of Physical Chemistry, Voronezh State University (Voronezh, Russian Federation).
https://orcid.org/0000-0002-7161-9754
zar-vrn@mail.ru

https://orcid.org/0000-0002-7085-1438
sg@chem.vsu.ru

https://orcid.org/0000-0003-2262-0131
kruzhilin.alexey@gmail.com

Evgenia A. Iлина, Graduate Student of the Department of Physical Chemistry, Voronezh State University (Voronezh, Russian Federation).
https://orcid.org/0009-0004-4825-5894
zhena.ali@yandex.ru