

Adsorption of sodium tridecanoate on copper from aqueous solutions and copper protection from atmospheric corrosion

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Abstract

The adsorption and protective effect of sodium tridecanoate $\text{CH}_3(\text{CH}_2)_{11}\text{COONa}$ (NaC_{13}) on copper and the possibility of increasing the effectiveness of protection by joint use with a trialkoxysilane (TAS) were investigated. A set of electrochemical, ellipsometric and corrosion tests was carried out on samples of M1 copper (copper content > 99.9%). From an analysis of the anodic polarization curves of copper from solutions containing NaC_{13} , it follows that when the inhibitor concentration is >0.07 mmol/l, the current density of copper active dissolution decreases and spontaneous passivation of the electrode occurs with a shift in the value of the pitting potential E_{pit} in the positive direction. With an increase in the concentration of the inhibitor, the value of E_{pit} increases while the anodic current density decreases. When the concentration of the inhibitor in the solution is 1.6 mmol/l or more, the value of E_{pit} shifts to the oxygen evolution region. Studies of NaC_{13} using the ellipsometric method showed that the adsorption of the inhibitor starts at very low concentrations, viz., 0.01 nmol/l. Adsorption is described by the Temkin equation with an adsorption free energy of 67 kJ/mol. In comparison with sodium oleyl sarcosinate $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CON}(\text{CH}_3)\text{CH}_2\text{COONa}$ (SOS) and sodium laurate $\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$ (NaC_{12}), adsorption begins at lower concentrations. Sodium tridecanoate adsorption on copper is polymolecular. Accelerated corrosion tests with daily moisture condensation on copper pretreated with an inhibitor solution at 60°C for 5 minutes were carried out. It was shown a protective mixture of NaC_{13} and TAS significantly increased the time until the appearance of the first corrosion site.

Key words: sodium tridecanoate, inhibitor, corrosion, passivity, adsorption, ellipsometry, copper.

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Currently, copper and its alloys are important structural materials that are widely used in heat exchange equipment, electrical devices and microelectronics. This is largely due to the properties of copper – low resistivity, high thermal conductivity and mechanical strength. Copper and copper alloys have relatively high corrosion resistance, but in a humid atmosphere or in aqueous solutions of corrosive salts they start to dull and corrode.

One of the effective methods to increase the resistance of copper that is widely reflected in monographs and scientific reviews [1–9] is to use organic corrosion inhibitors

(CI). Many CIs form thin films on the surface of copper that can reliably protect it from corrosion in neutral environments, including a humid atmosphere.

One of the most effective and popular classes of copper CIs are azoles, in particular, 1,2,3-benzotriazole and its derivatives [2–8]. Carboxylic acids and their salts, which differ from azoles in greater environmental safety and availability, can also serve as copper CIs [1, 9–14]. Generally, their higher homologs are more effective. They have increased hydrophobicity, which contributes to their better adsorption from aqueous solutions. However, with an increase in the chain length of carboxylates, their critical micelle concentration (CMC) decreases, which may reduce the adsorption of CI anions from an aqueous solution.

It is known [15–17] that corrosion protection by ultrathin coatings formed by carboxylates on some metals (zinc, aluminum alloys) can be improved by joint use with various trialkoxysilanes (TAS).

The purpose of this work is to study the adsorption of the sodium salt of tridecanoic acid $\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$ (NaC_{13}) on copper and the protection of this metal from atmospheric corrosion, as well as the possibility of increasing its efficiency by the joint use of the carboxylate CI with TAS.

Experimental

Electrochemical, ellipsometric, and corrosion tests were performed on samples of M1 copper ($\geq 99.9\%$ copper). Inhibitor solutions were prepared by dissolving tridecanoic acid in water followed by neutralizing it with an equivalent amount of NaOH. The borate buffer solution with pH 7.36 containing 10 mmol NaCl served as the background solution.

A sample for electrochemical studies was made as a cylindrical copper electrode embedded in a Teflon holder. The working surface of the electrode was the base of the cylinder with an area of 0.75 cm^2 . The working surface was cleaned successively with an abrasive paper with grit P600 and P1000, degreased with acetone, and further treated with magnesium oxide on felt until a drop of water covered the entire working surface of the electrode.

Anodic polarization curves (APC) of copper were recorded in a glass three-electrode cell with electrode spaces separated with a glass filter, using an IPC-Pro MF potentiostat. A silver/silver chloride reference electrode and a graphite auxiliary electrode were used. All measured electrode potentials were recalculated to the normal hydrogen scale. The electrode was placed in a cell with 60 ml of the background solution and kept for 15 minutes at $E = -0.6 \text{ V}$ in order to reduce the primary copper oxide formed in air. After that, polarization was turned off for 15 minutes. During this time, the free corrosion potential ceased to change and assumed a specific value, after which the electrode was anodically polarized at a potential scan rate of 0.2 mV/s .

The adsorption of NaC_{13} from borate buffer with pH 7.4 on a copper electrode was studied by the reflective ellipsometry method (REM) in a specially designed cell that

allows electrochemical and ellipsometric studies to be conducted simultaneously. The method and application of REM for studying the adsorption of organic compounds on copper are detailed in [18]. The ellipsometric experiment involved measuring the phase angle Δ and polarization angle ψ of light reflected from the electrode surface.

It follows from the REM theory that the changes in the ellipsometric angle $\delta\Delta$ are proportional to the thickness of the growing film d within 10 nm. There is a relationship between the experimentally determined changes in the Δ angle and the degree of coverage of the surface with inhibitor particles (θ) at various concentrations C_{in} of the adsorbate in the solution:

$$\theta = \beta\delta\Delta = \beta(\Delta - \Delta_0), \quad (1)$$

where β is the parameter determined from the experimental dependence on the specifically selected adsorption isotherm of the adsorbate, Δ_0 is the angle related to the original surface, and Δ is the current angle. A platinum auxiliary electrode and a RUDOLPH RESEARCH ellipsometer were used. A helium-neon laser with a wavelength of 640 nm served as the radiation source.

The plot of $|\delta\Delta|$ variation *versus* $\lg C_{in}$ was converted to the adsorption isotherm. The experimental curve in the range of medium degrees of coverage (θ) is described by the Temkin logarithmic isotherm:

$$\theta = 1/f(\ln B_{max}C), \quad (2),$$

where f is the surface energy inhomogeneity factor and B is the adsorption equilibrium constant related to the free adsorption energy ($-\Delta G_A^0$) by the relationship $B = [\exp(-\Delta G_A^0 / RT)] / 55.5$.

To perform an ellipsometric experiment, an electrode was cleaned on abrasive paper to the mirror surface, then polished on felt impregnated with calcium oxide. The criterion for preparing the electrode at this stage was that a drop of water covered the entire copper surface and held onto it. The electrode was placed in a cell and kept for 30 min at $E = -0.6$ V to restore the primary oxide film, then E was switched to 0.00 V and the electrode was oxidized for 1.5 hours to stabilize its surface. After 1.5 hours, the Δ angle ceased to change. This was taken for surface stabilization and a CI concentrate was introduced into the cell, after which the Δ angle was measured. By conducting these experiments with different inhibitor concentrations C_{in} , we obtained the plot of Δ *versus* $\lg C_{in}$.

Corrosion tests were carried out in cells with a volume of 0.5 liters, at the bottom of which 50 ml of hot water (60°C) was poured. Preliminarily, copper samples (plates with a size of 30×70 mm) were polished on abrasive paper with grit P1000 to a mirror finish and degreased with acetone. Then they were kept in an aqueous solution of an inhibitor with a temperature of $t = 60^\circ\text{C}$ for 5 min. After that, the cell was closed with a lid on which the copper samples were hung. As a result of the natural cell cooling, water vapor condensed on the walls and on the samples. Every day the cooled water was replaced by hot water.

The samples were examined daily to determine the time until the first signs of copper corrosion.

Results and Discussion

Figure 1 shows the isotherm of the changes in Δ angle *versus* $\lg C_{\text{in}}$ for NaC_{13} , oleyl sarcosinate $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CON}(\text{CH}_3)\text{CH}_2\text{COONa}$ (SOS) and sodium laurate $\text{C}_{11}\text{H}_{23}\text{COONa}$ (NaC_{12}). Studies of NaC_{13} adsorption by the ellipsometric method showed that the adsorption of this inhibitor on oxidized copper surface begins at somewhat lower concentrations than in the case of NaC_{12} adsorption. This could be expected, given that the hydrophobic alkyl radical in the case of NaC_{13} is by one methylene group larger than NaC_{12} . After the formation of a conditional monolayer indicated by a plateau on the plot of $(-\delta\Delta)$ *versus* $\lg C_{\text{in}}$ for NaC_{13} , the Δ angle continues to change, which is characteristic of further polymolecular adsorption.

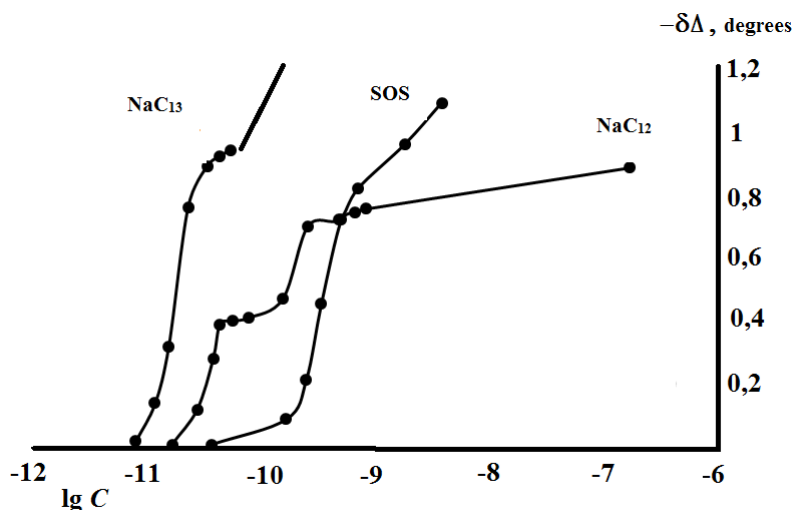


Figure 1. Isotherms of the ellipsometric angle Δ variation upon the adsorption of sodium tridecanoate, sodium oleyl sarcosinate and sodium laurate on Cu at $E = 0.0$ V.

To describe the adsorption in the range of medium θ of the monomolecular layer nearest to the copper surface, the logarithmic Temkin isotherm is applicable (2). Calculations for NaC_{13} gave the value $(-\Delta G_{\text{A}}^0) = 67 \pm 3$ kJ/mol. Comparison of the results of NaC_{13} adsorption measurements with those of the best CIs of the fatty series studied previously (SOS and NaC_{12}) suggests the important role of the hydrophobicity of the anion in its adsorption on oxidized copper. The hydrophobicity of organic molecules is estimated by the logarithm of the distribution coefficient $\lg P$ that is calculated from the data on the distribution of the chemical compound in the system of two immiscible liquids, octanol–water [19]. The surface activity of anions of organic acid salts depends on the pH of aqueous solutions, therefore, their hydrophobicity is characterized by the $\lg D$ value, hydrophobicity constant of the dissociated form, which is calculated taking into account

the pK_a of the corresponding acids, where $\lg P$ is the hydrophobicity constant of the neutral compound [20]:

$$\lg D = \lg P - \lg [1 + 10^{(pH - pK_a)}] \quad (4)$$

It is quite expected that NaC_{12} anions are inferior in adsorption capacity to their NaC_{13} analogues for the above reasons. The most hydrophobic OCH anions are very close in size ($-\Delta G_A^0$) to the anions of lauric acid (almost equal within the reproducibility of the measurements). However, their protective effect, which is manifested in the stabilization of the passive state of copper, *i.e.* the value $\Delta E = E_{\text{pit}}^{\text{in}} - E_{\text{pit}}^{\text{background}}$ calculated from the anodic polarization curves, shows that SOS is a more effective CI than NaC_{12} . It can be assumed that the mechanism of protection of passive copper from the corrosive action of the chloride ion by SOS anions and sodium alkyl carboxylates is not quite the same. It is possible that the SOS radical creates conformational difficulties in the formation of a compact adsorption layer on copper. In this regard, of particular interest is a comparison of the effect of the two nearest homologues (NaC_{12} and NaC_{13}) on the anodic dissolution of copper in borate buffer containing 10 mM NaCl.

From the anodic polarization curves of copper in borate solutions containing NaC_{13} , it can be seen that at $C_{\text{in}} > 0.07$ mmol/l, the current density of active dissolution of copper decreases and spontaneous passivation of the electrode occurs with a shift of the E_{pit} value in the positive direction (Figure 2). With an increase in C_{in} , the value of E_{pit} increases and the anodic current density decreases. If the inhibitor concentration in the solution is up to 1.6 mmol/l or more, the value of E_{pit} shifts to the oxygen evolution region.

The difference ΔE between the E_{pit} measured in solutions containing an inhibitor and in the background is considered to be a measure of the effectiveness of the inhibitor in the ability to stabilize the passivation of metal electrodes. Table 1 shows a comparison of the effectiveness of NaC_{13} with that of NaC_{12} and SOS. As follows from the table, an increase in the length of the hydrocarbon radical (by a $-\text{CH}_2-$ moiety) significantly shifts the E_{pit} in the anodic direction at the same C_{in} .

Table 1. Physicochemical characteristics ($\lg P$, pK_a , $\lg D$), protective effects and parameters of adsorption of corrosion inhibitors on copper in borate buffer with pH 7.4. The results for SOS and NaC_{12} were obtained previously [13, 14].

Inhibitor	ΔE , V at $C_{\text{in}} = 1.6$ mmol/l	$(-\Delta G_A^0)$, kJ/mol	$\lg P$	pK_a	$\lg D$ at pH 7.4
SOS	0.44	62 ± 3.0	7.00	3.77	3.61
NaC_{12}	0.25	64 ± 3.0	5.03	4.78	2.41
NaC_{13}	0.90	67 ± 3.0	5.56	4.78	2.97

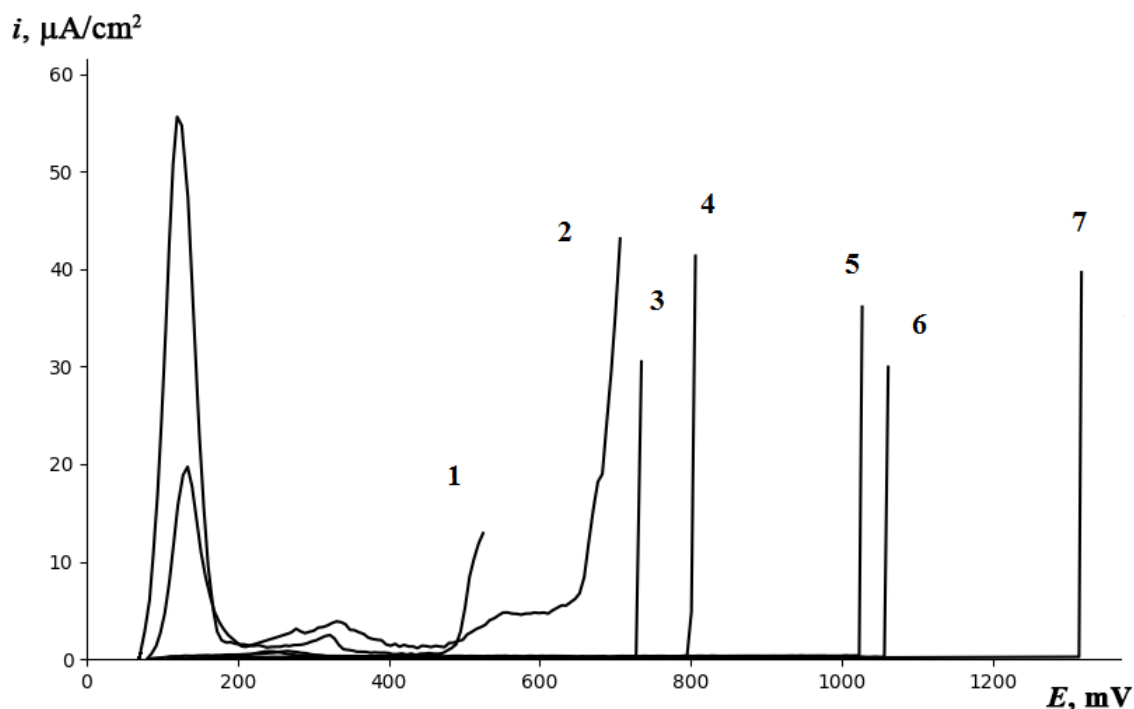


Figure 2. Anodic polarization curves of copper in borate buffer solution with pH 7.4, in the presence of 10 mmol NaCl with sodium tridecanoate as CI (mmol/l): 1 – background; 2 – 0.07; 3 – 0.14; 4 – 0.24; 5 – 0.68; 6 – 1.3; 7 – 1.6.

Severe accelerated corrosion tests in a humid atmosphere with daily condensation of moisture on copper samples showed that their five-minute passivation with inhibitor solutions at elevated temperatures, *i.e.* $t = 60^{\circ}\text{C}$, is more effective than at room temperature. This is especially apparent in copper passivation in a solution of NaC_{12} synthesized from technical lauric acid. Probably, it contains impurities of other alkanecarboxylic acids that enhance the passivating effect of laurate anions.

As already noted above, the passivating effect of higher carboxylates toward certain metals can be enhanced by combining them with small additions of TAS. Indeed, despite the fact that aminoethylaminopropyltrimethoxysilane itself (AEAPTS) does not protect copper from corrosion, an aqueous solution of its combination with NaC_{13} can be effective in passivating this metal. This is indicated already by the anodic polarization curves of copper shown in Figure 3.

Corrosion tests with daily condensation of moisture from passivated copper samples (Table 2) showed that the efficiency of this formulation with $C_{\text{in}} = 8.0$ or 16 mM that forms ultra-thin protective films significantly exceeds that of films formed by NaC_{12} or NaC_{13} .

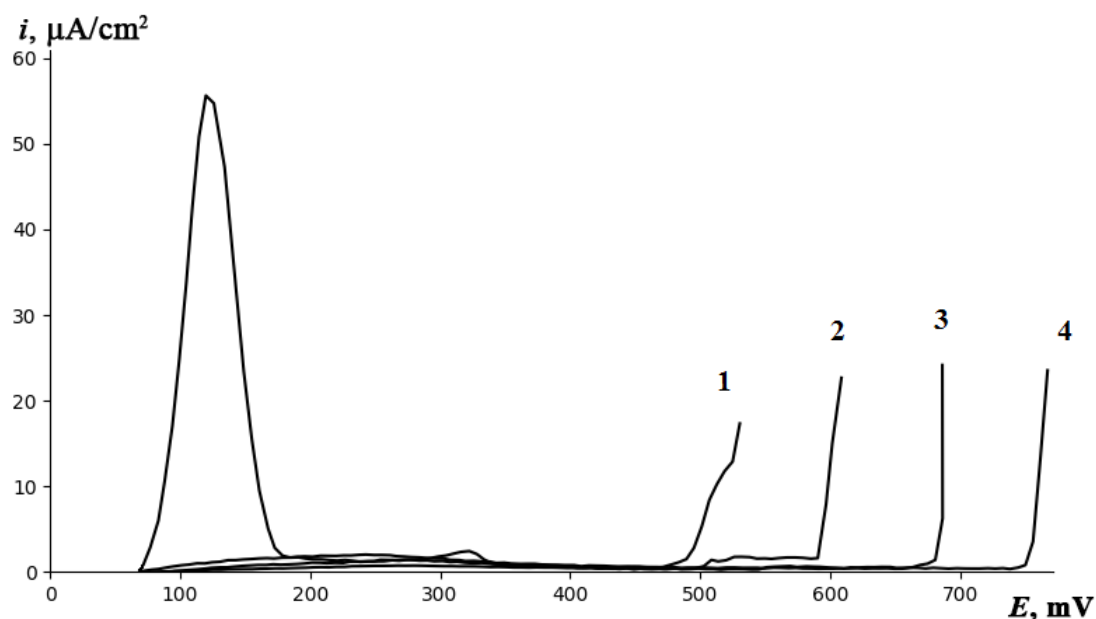


Figure 3. Anodic polarization curves of copper after keeping the electrode in the inhibitor solution for 5 minutes with 60°C in borate buffer solution with pH 7.4, in the presence of 10 mmol NaCl. Inhibitor mixture – sodium tridecanoate and TAS (mol/l): 1 – background; 2 – 1.5 + 0.5; 3 – 6 + 2; 4 – 12 + 4.

Table 2. The results of corrosion tests of copper in a humid atmosphere with daily moisture condensation on samples pretreated in passivating aqueous solutions of organic corrosion inhibitors.

Passivating solution of CI (concentration in mmol/l)	Time until the appearance of corrosion (days) on copper after its passivating treatment at 60°C for 5 minutes
Without inhibitor	1.2±0.3
SOS, 2.0	23±0.5
NaC ₁₂	
2.0	20±0.5
8.0	46±0.5
16.0	65±0.5
NaC ₁₃	
2.0	13±0.5
8.0	19±0.5
16.0	24±0.5
NaC ₁₃ +AEPTS	
6.0+2.0	62±0.5
12.0+4.0	75±0.5

Conclusions

1. Sodium tridecanoate inhibits the active dissolution of copper in a neutral aqueous solution at $C_{in} = 0.14$ mmol/l and shifts the pitting potential to the oxygen evolution potential at a concentration of 1.6 mmol/l.
2. The adsorption of sodium tridecanoate on copper at $E = 0.0$ V is polymolecular. The formation of the first monolayer inhibitor, already starting from a very low concentration (0.01 nmol/l), is described by the Temkin equation with a relatively high free energy of adsorption ($-\Delta G_A^0$) = 67 kJ/mol, which suggests the possibility of chemisorption of tridecanoate.
3. Accelerated corrosion test of copper pretreated with an CI solution, in a humid atmosphere with daily moisture condensation on samples, showed that sodium tridecanoate is inferior in protective properties to some other inhibitors, but when it is used in combination with TAS at a molar ratio of 3:1, the protective properties are improved significantly.

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