Corrosion inhibition of copper and its alloy MNZh5-1 by salts of succinic and alkenylsuccinic acids in chloride solution¹

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Abstract

The adsorption, protective and passivating effect of sodium salts of succinic, itaconic and a blend of alkenylsuccinic acids (SKAP-25) on the oxidized surface of copper and copper–nickel alloy MNZh5-1 in neutral buffer and chloride solutions was studied. The adsorption of sodium succinate and itaconate is adequately described by the full Temkin isotherm equation with the value of the free energy of adsorption ($-\Delta G_a^0$) on oxidized copper at $E=0.0$ V being 77.4 and 65.4 kJ/mol, respectively. The values of ($-\Delta G_a^0$) for these corrosion inhibitors on the pre-oxidized MNZh5-1 alloy electrode are 89.3 and 58.3 kJ/mol, respectively. Such values of ($-\Delta G_a^0$) suggest chemisorption interaction of these organic anions with the oxidized surface of copper and its alloy. Corrosion tests of copper and alloy MNZh5-1 in solutions for 7 days showed that a formulation of SKAP with the sodium salt of 2-mercaptobenzothiazole with a 7.1:1.0 mass ratio of the components was the best corrosion inhibitor.

Keywords: *copper, MNZh5-1 alloy, dicarboxylates, adsorption, neutral chloride media, ellipsometry, Temkin isotherm.*

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Introduction

Copper and copper-based alloys are structural materials and are actively used in many industries. Due to its high thermal conductivity and electrical conductivity, copper is currently used in renewable energy systems. Copper alloys are widely used in jewelry, monuments, electrical products, and heat exchangers. Despite the relatively high corrosion resistance of copper in many environments, including humid atmospheres, it corrodes with a patina.

In this regard, the task of improving the protection of copper and its alloys against corrosion remains relevant. One simple and affordable way to protect metal from corrosion

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is to introduce organic corrosion inhibitors (CI) into the environment in which it is located. For this purpose, substances of azoles class are often used, for example, 1,2,3-benzotriazole (BTA), 2-mercaptobenzothiazole (2-MBT) and others [1–10].

In addition to azoles and their derivatives, salts of carboxylic acids are widely known as CIs of copper and its alloys [11–14]. Compared to azoles, these compounds are cheaper and less environmentally hazardous.

Earlier we studied the adsorption and protective properties of a number of carboxylates [14] and showed that the most effective are sodium oleate and sodium oleoylsarcosinate. On oxidized copper at $E=0.0$ V the values of their free energy of adsorption ($-\Delta G_a^0$) are 62 and 57 kJ/mol, respectively. At the same time, dicarboxylic acids and their salts are studied relatively poorly, although interest in them, as the CIs of various metals in neutral environments and in the protection against atmospheric corrosion periodically arises [13–16]. This is due to the assumption that in the presence of two reactive carboxyl groups in their molecules, the adsorption energy value of dicarboxylates may be higher than that of monocarboxylates. Consequently, they can show higher protective and passivating properties.

Dicarboxylates have been studied extensively for the protection of mild steel and much less frequently for other metals [12–21]. A. Mercer [22] showed that dicarboxylates can be more effective than alkyl monocarboxylates. However, later German researchers [18], studying the effect of mono- and dicarboxylates on the passivation of mild steel in a 0.01 M solution of potassium nitrate at pH 7.50, noticed that its transition into a passive state occurs after different times. Thus, in a solution of sodium sebacinate or its mixture with caprylate, the passive state is established after 10–15 min of immersion of the electrode in it. In a solution of azelate or its mixture with pelargonate, passivation of soft steel is achieved not earlier than 25 min. According to the results of electrochemical impedance spectroscopy (EIS) measurements, the resistance of the R_{ad} adsorption layer for dicarboxylates is lower than for monocarboxylates, which is due to the lower adsorption capacity of dicarboxylates.

K. Aramaki [17] suggested that α,ω -dicarboxylates with carbon atoms in alkylene $n_C=7$ and 8, are adsorbed on the surface of iron oxide due to two carboxyl groups, thus forming a loop. This position is disadvantageous for the formation of a tightly packed layer, whereas monocarboxylates with their long alkyl can create it by placing their alkyls almost perpendicular to the surface during adsorption. As a result, such an adsorption layer acts as a barrier to aggressive components of the medium. Comparing the results of EIS measurements, one can conclude that the higher the R_{ad} value, the denser the adsorption layer is packed.

The authors [19] studied not only dicarboxylates themselves, but also their mixtures with BTA on mild steel in 0.02 M NaCl aqueous solution. They found that nontoxic dicarboxylates with $n_C < 4$ spontaneously passivate soft steel in chloride solution. These CIs inhibit the anodic reaction but have little or no effect on the cathodic reaction. The effectiveness of such dicarboxylates ($n_C > 4$) increases if their mixtures with BTA are used,

e.g. a high degree of steel corrosion inhibition is observed for a mixture of sebacinate with BTA.

In our work we studied dicarboxylate salts which are derivatives of succinic acid: sodium itaconate contains $=CH_2$ -group and SKAP – relatively long hydrocarbon chains, also including one double bond ($n_C = 12–15$). These substituents are not located between carboxy groups in the hydrocarbon chain, but are attached to one of their binding methyl groups.

Adsorption, passivation and protective properties of sodium succinate, sodium itaconate and sodium salts of acids contained in the product known as KAP-25 [24] were studied on copper and its alloy MNZh5-1 in a neutral chloride solution.

Experimental

Working electrodes are made of M1 copper and MNZh5-1 alloy, containing in %: 90.6–93.7 Cu; 5.0–6.5 Ni+Co; 1.0–1.4 Fe; 0.3–0.8 Mn; ≤ 0.5 Zn; ≤ 0.15 Si; ≤ 0.1 Sn; ≤ 0.04 P; ≤ 0.01 S [25].

We used in our research commercial compounds – succinic (CAS Number 110-15-6, Sigma Aldrich) and itaconic (CAS Number 97-65-4 Acros Organics) acids, and also KAP-25 (TU 2499-080-05015207-2003 Antirust additive KAP-25 from May 20, 2003, OAO PO TOS).

Sodium salts of succinic and itaconic acids were prepared by the neutralization reaction with sodium hydroxide solution. The exact composition of the additive KAP-25 is unknown, so the amount of alkali needed to convert acids from its composition into salts was taken from the acid number listed in the product data sheet, namely 382 mg/g KOH. Because the exact composition of KAP-25 is unknown, the product obtained after its neutralization is referred to in the article as SKAP-25, and its concentration is given in g/L. The concentration of the substance in the working solution was 33.7 g/L. The pH values of SKAP-25 working solutions were maintained between 6.7 and 7.4.

For ellipsometric measurements, sodium succinate and itaconate solutions with the concentration $C_{in} = 10^{-8}–10^{-10}$ M were used; for electrochemical and corrosion studies, 0.05 and 0.1 M concentrates were used.

Studies of adsorption on the oxidized surface of copper and alloy were carried out on a manually operated RR 2000 ellipsometer with an electrochemical cell, which simultaneously allows to maintain the electrode potential E set from the potentiostat and measure the ellipsometric phase angle. The accuracy in determining the angle is $\pm 0.05^\circ$. Potentials of the electrode in solution, E , were measured relative to the silver chloride reference electrode; their values are given in the article in terms of a standard hydrogen electrode. The potential of the oxidized electrode surface for copper and alloy $E = 0.0$ V (SHE).

For a homogeneous film thickness $d \leq 10$ nm, the Drude equation is valid, which allows us to pass from changes to the degree of surface coverage [26]:

$$d = -\alpha \delta \Delta = -\alpha (\Delta - \Delta_0) \quad (1)$$

where α is a proportionality coefficient, Δ_0 is the value of the angle for the initial surface, and Δ is the value of the angle during the experiment. If adsorption occurs, then $\delta\Delta = (\Delta - \Delta_0) < 0$.

To obtain the isotherm of CI adsorption on the pre-oxidized electrode at $E = 0.0$ V, its concentrate was added in portions to the cell with borate buffer solution pH 7.4. For each C_{in} , the angle Δ decreased in time and stopped changing after 60–90 min. Thus, we determine the angle difference ($-\delta\Delta$) to plot its dependence on C_{in} . The value of S_{in} , at which the angle change stops, corresponds to a certain degree of coverage θ . C_{in} , at which the value ($-\delta\Delta$) stops changing, corresponds to the concentration of the formation of the first monolayer, *i.e.*, $\theta \rightarrow 1$ [27, 28]. The experimental dependence of the angle Δ change on $\log C_{in}$ is reconstructed into the adsorption isotherm $\theta = f(\ln C)$ and the adsorption free energy ($-\Delta G_a^0$) is calculated.

The adsorption of these compounds is adequately described by the full Temkin equation:

$$\theta = \frac{1}{f} \ln \frac{1 + B_{\max} C}{1 + B_{\min} C} \quad (2)$$

where f is the surface heterogeneity factor characterizing the change in the enthalpy of adsorption with surface coverage; $B_{\max}$ and $B_{\min}$ are the adsorption equilibrium constants corresponding to the highest and lowest values of adsorption energy. The value of B is related to the free energy of adsorption ($-\Delta G_a^0$) by the relation:

$$B_{\max,(\min)} = \exp[(-\Delta G_{a,\max(\min)}^0) / RT] \quad (3)$$

When determining ($-\Delta G_{a,\max}^0$), ($-\Delta G_{a,\min}^0$), f -factor, $B_{\max}$, and $B_{\min}$, we used the technique described earlier in [29].

Electrochemical studies consisted in recording anodic polarization curves in borate buffer solution with the addition of 0.01 M NaCl and different concentrations of CI. They were obtained on electrodes made of copper and alloy MNZh5-1 in an electrochemical cell with separated electrode spaces on an IPC-PRO MF potentiostat (RF). The working electrode was preliminarily roughened on sandpaper of different grit 400–1000 and degreased with acetone.

After removal of air formed film of metal oxides on the alloy (by keeping the electrode for 15 min in borate buffer with pH 7.4 and 0.01 M NaCl at $E = -0.60$ V) the potentiostat was turned off till establishment of free corrosion potential E_{cor} . After establishing a new value of E_{cor} formed by adsorption of organic CI molecules introduced into the buffer solution on the electrode, the potentiostat was connected again and polarization curves were recorded at the rate of potential sweep of 0.2 mV/s.

The potential of local metal depassivation by chlorides, E_{pt} , was determined by a sharp increase in current on the polarization curve followed by visual identification of pitting on the surface of the electrode. The error in the measurement of E_{pt} is 0.01 V. The protective effect of the copper and alloy local depassivation inhibitor was estimated by the magnitude

of the increase in E_{pt} caused by its introduction into the background solution, *i.e.*, $\Delta E = E_{pt}^{in} - E_{pt}^{bg}$.

Corrosion studies of copper and its alloy were carried out in distilled water containing 0.01 M NaCl or 3.5% NaCl and different C_{in} . Metal plates of dimensions $50 \times 30 \times 3$ mm were cleaned on abrasive paper of different grit (from 240 to 1000), degreased with acetone and weighed before the experiment. Accuracy of weighing was ± 0.0002 g. Samples were then placed in chloride solutions with dicarboxylates of different C_{in} at room temperature $t = (22 \pm 2)^\circ\text{C}$ and natural aeration of the solution. After 7 days, the plates were removed, cleaned of corrosion products, and weighed again. According to the difference in mass of the plate before and after the test, the corrosion rates in the background (K_0) and inhibited solution (K_{in}) were calculated and the degree of protection of copper Z was determined by the formula:

$$Z = \frac{K_0 - K_{in}}{K_0} \cdot 100\% \quad (4)$$

A mixture of these substances with concentrations of 0.2157 g/L and 0.0302 g/L was prepared for corrosion tests of copper with SKAP-25 composition and MBT sodium salt, respectively.

Results and Discussion

The adsorption of sodium succinate on the pre-reduced ($E = -0.60$ V) and oxidized ($E = 0.0$ V) copper surface was studied earlier in pure borate buffer at pH 7.4 [30]. These studies were carried out by ellipsometric method, by obtaining the adsorption isotherm and from it determining the values ($-\Delta G_a^0$) and f , characterizing the adsorption capacity of compounds. Adsorption of sodium succinate on an oxidized copper surface occurs in the region of very low C_{in} and is described by Eq. (2) with the value $-\Delta G_{a,max}^0 = 77.4$ kJ/mol, which is 30 kJ/mol higher than for its lower homologue sodium malonate. It is interesting, that on the copper electrode free from oxide film at $E = -0.60$ V the ($-\Delta G_{a,max}^0$) values for these compounds are much less (53.1 and 38.3 kJ/mol respectively) but succinate adsorption remains strong enough to consider its interaction with the surface as chemisorption. Indeed, polarization measurements on copper at a concentration of 3 mmol/L of the above sodium salts of dicarboxylic acids on anodic dissolution of the metal in borate buffer containing 0.01 M aggressive NaCl showed that the protective capacity of succinate is higher than that of sodium malonate.

Electrochemical studies

Additions of sodium succinate to borate–chloride solution at $C_{in} = 0.5$ mmol/L reduce the current density of anodic passivation copper i_p and increase E_{pt} on Cu samples by almost 0.30 V [23]. However, increasing C_{in} to 1.0 mmol/L increases the passivation current

density i_p , and further growth of C_{in} to 5.0 mmol/L, although it improves the ability of sodium succinate to stabilize the passive copper state, but i_p reaches $120 \mu\text{A}/\text{cm}^2$, which indicates the formation of its anions soluble complexes with Cu(I), preventing passivation of the electrode.

Sodium itaconate behaves differently from succinate (Figure 1). At the content of 0.25 mmol/L of this CI in the working solution there is no suppression of the copper anodic dissolution peak and the i_p shifts to a more negative region. When C_{in} is increased to 2 mmol/L, E_{pt} increases, but i_p also increases, from which it can be concluded that soluble complexes with Cu(I) are formed. A similar situation was observed when sodium succinate C_{in} was increased, but up to 5 mmol/L.

Figure 1. Anodic polarization curves of copper in borate buffer solution with pH 7.4 containing 0.01 M NaCl without (1) and with addition of sodium itaconate (in mmol/L): 2–0.25, 3–0.5, 4–1, 5–2, 6–5.

However, further increase in the sodium itaconate C_{in} leads to almost complete suppression of the anodic dissolution peak. At the same time, the free corrosion potential E_{cor} and E_{pt} increase in comparison with $C_{in}=2$ mmol/L. The difference in the behavior of sodium succinate and itaconate at the same C_{in} can be explained by the presence of a methylene group and a double bond in the structure of the latter. Probably, the anion of itaconate under certain conditions is able, at least, to dimerize with breaking the double bond, which increases the hydrophobicity of this CI.

In contrast to copper, spontaneous passivation in the presence of sodium succinate occurs on alloy MNZn5-1 at $C_{in}=0.25$ mmol/L, *i.e.* the first peak of i_p is suppressed and E_{pt} increases (Figure 2a). When C_{in} increases up to 1.5 mmol/L, the E_{pt} value increases, reaching

0.91 V, but at $C_{in}=2$ mmol/L it decreases to 0.69 V. It can be assumed that increasing C_{in} succinate anions begin to form water-soluble complexes with metal cations included in the alloy, which weakens their ability to stabilize passivation of MNZh5-1. In this case, spontaneous passivation of the alloy is not disturbed and the second peak of the anodic current density only slightly increases, so we can assume that soluble complexes are not formed with Cu(II) cations. However, at 5 mmol/L, unlike 2 mmol/L, the E_{pt} does not decrease and the i_p of the first peak of anodic dissolution increases, which confirms the formation of succinate ion complexes with Cu(I).

Figure 2. Anodic polarization curves of alloy MNZh5-1 in borate buffer solution of pH 7.4 containing 0.01 M NaCl without (1) and with addition at C_{in} (in mmol/L) a) sodium succinate: 2 – 0.25; 3 – 0.5; 4 – 1.0; 5 – 1.5; 6 – 2.0; 7 – 5; b) Sodium itaconate: 2 – 0.13; 3 – 0.25; 4 – 1.0; 5 – 1.5; 6 – 2.0; 7 – 5.0; c) $C_{SKAP-25}$ (g/L): 2 – 0.0843; 3 – 0.1685; 4 – 0.337; 5 – 0.573.

Sodium itaconate at low $C_{in}=0.13$ mmol/L increases the i_p of the first peak by 2.5 times compared to the background curve without enrichment of E_{pt} (Figure 2b). Increasing to $C_{in}=0.25$ mmol/L leads to spontaneous passivation of the electrode, but without increasing E_{pt} . All subsequent studied C_{in} up to 5 mmol/L lead to an increase in E_{pt} . For $C_{in}=1$ mmol/L

the protective effect of $\Delta E = 0.04$ V, and for $C_{in} = 1.5$ and 5 mmol/L 0.07 and 0.23 V, respectively. Sodium itaconate in the region of concentrations $C_{in} = 0.13$ –2 mmol/L suppresses the first and second peaks of anodic dissolution, but at $C_{in} = 5$ mmol/L both peaks are present, similarly to what happens when sodium succinate is introduced at the same concentration. This fact again confirms that itaconium ions can also form water-soluble complexes with Cu(I) and Cu(II) cations when C_{in} is increased.

According to [23], a mixture of substituted sodium alkenylsuccinate – SKAP-25 compounds at a concentration of 0.057 g/L reduces the i_p of the first peak on copper by a factor of 10 and increases the E_{pt} to 0.76 V. As SKAP-25 increases up to 2.359 g/L, the E_{pt} increases and reaches the oxygen release potential ($E = 1.2$ V). It is obvious that SKAP-25 is much more effective as an inhibitor of anodic dissolution of copper, succinate and itaconate sodium. This is due to the presence in its composition of hydrophobic anions with increased surface activity and their complex compounds with copper cations, if formed, are insoluble in aqueous solution. In this regard, we investigated the possibility of using SKAP-25 to protect the alloy MNZn5-1 in neutral solutions containing sodium chloride.

Anodic polarization curves of the MNZn5-1 alloy obtained in borate buffer containing 10 mmol/L NaCl and SKAP-25 additives are shown in Figure 2c. All studied SKAP-25 additives suppress the first and second i_p peaks of the alloy and can increase the protective effect, which is expressed in the increase of E_{pt} of the sample. Thus, at $C_{SKAP-25} = 0.57$ g/L the passive state of the alloy is preserved in a wide range of potentials and the E_{pt} exceeds 1.25 V, which on copper is achieved according to [23] at C_{in} of this CI is 4 times higher.

Ellipsometric studies

Since spontaneous passivation of copper and alloy MNZn5-1 is caused by adsorption of dicarboxylic acid anions on their surface, its evaluation was carried out by ellipsometric method in pure borate buffer pH 7.4 at constant $E = 0.0$ V. In these experiments, the ellipsometric phase angle Δ stopped changing when the electrode was oxidized for 40–50 min. This allowed us to attribute the changes of Δ to the adsorption of dicarboxylate anions when injected into the solution of CI.

On the oxidized copper surface adsorption of sodium succinate ($\log D = -5.47$), despite their high hydrophilicity (Table 1), occurs in the region of very low C_{in} (Figure 3a). Apparently, this is due to the formation of a chelate complex with copper cations on the electrode surface. When the double bond is introduced into the sodium succinate structure, adsorption on oxidized copper also changes: sodium itaconate adsorbs at concentrations 2 orders of magnitude higher than sodium succinate. This is due to its higher hydrophilicity than succinate (Table 1).

The values ($-\Delta G_{a,max}^0$) of the studied anions calculated by the full Temkin isotherm (Eq. 2) for sodium succinate and itaconate are 77.4 and 65.4 kJ/mol, respectively (Figure 3a, Table 2). The adsorption of sodium itaconate on copper starts from $C_{in} = 0.1$ nmol/L and reaches the limit of surface coverage when $C_{in} = 1$ nmol/L is reached. The appearance of a

multiple bond in the structure of sodium itaconate sharply reduces its adsorbability on the oxidized copper surface in neutral buffer solution as compared to succinate itself. This is explained by the increased hydrophilicity of the itaconate anion compared to succinate and its lower surface activity. In spite of this, itaconate chemisorbs on copper, although the surface complexes it forms are apparently less stable.

Table 1. Physicochemical characteristics of dicarboxylic acids: acid dissociation constants pK_a , log distribution coefficients ($\log P$). Values of pK_a , $\log D$ and $\log P$ were obtained from chemicalize.com.

Dicarboxylic acid	$\log P$	$\log D$	pK_a
Succinic acid $\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$	-0.40	-5.47	3.55; 5.69
KAP-25*			
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_5-\text{CHCH}_2(\text{COOH})_2$	4.23	4.36	4.82
$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7-\text{CHCH}_2(\text{COOH})_2$	6.01	4.39	4.82
Itaconic acid $\text{HOOC}-\text{CH}_2(\text{C}=\text{CH}_2)\text{COOH}$	0.053	-6.25	3.56; 4.37

*The main substances included in the KAP-25 are given.

Table 2. Adsorption characteristics of isotherms for sodium succinate and itaconate on the surface of copper and MNZh5-1 at the potential $E = 0.0$ V: minimum and maximum values of B , $-\Delta G_a^0$, and factor f .

Inhibitor	Metal	$B_{i,\max}$ L/mol	$B_{i,\min}$ L/mol	$-\Delta G_{a,\min}^0$, kJ/mol	$-\Delta G_{a,\max}^0$, kJ/mol	f
Sodium succinate	Copper	$6.7 \cdot 10^{11}$	$1.5 \cdot 10^{11}$	73.7	77.4	1.49
	MNZh5-1	$8.3 \cdot 10^{13}$	$2.3 \cdot 10^{13}$	86.1	89.3	1.26
Sodium itaconate	Copper	$5.26 \cdot 10^9$	$8.95 \cdot 10^8$	61.0	65.4	1.76
	MNZh5-1	$3 \cdot 10^8$	$7.2 \cdot 10^7$	54.7	58.3	1.43

The adsorption of succinate anions on MNZh5-1 alloy begins at C_{in} 2.5 orders of magnitude lower than on copper (Figure 3b). It is adequately described by the equation of full Temkin isotherm with greater value ($-\Delta G_{a,\max}^0$) = 89.3 kJ/mol and smaller value f = 1.26 than on copper (Table 2).

On the contrary, the adsorption of sodium itaconate on the oxidized alloy surface weakens, and the monolayer coverage of the surface occurs at C_{in} = 10 nmol/L. The value ($-\Delta G_{a,\max}^0$) calculated from Eq. (2) is 58.3 kJ/mol (Table 2), which suggests its chemisorption, although weaker than that of succinate. The adsorption on the oxidized alloy

in the case of sodium itaconate is characterized by a polylayer coverage of the surface shown by dashed lines in Figure 3b.

Figure 3. Dependence of the change in the ellipsometric angle ($-\delta\Delta$) on the logarithm of the concentration of dicarboxylic acid anions in borate buffer solution with pH 7.4: (a) sodium succinate (1) and sodium itaconate (2) on an oxidized copper surface at $E = 0.0 \text{ V}$ in borate buffer solution with pH 7.

b) Sodium succinate (1), sodium itaconate (2) on the oxidized surface of the alloy MNZn5-1. The dotted line shows the polymolecular adsorption

Protective properties of the mixture of sodium salts KAP-25 and MBT

Earlier in our works [23, 31] small additives of sodium salt of 2-mercaptobenzothiazole (SMBT) were used to enhance the protective effect of dicarboxylates. According to impedance measurements [23], the SKAP-25 + SMBT mixture (7.1:1 by weight) exhibited high protective properties against copper in an aqueous solution of 3.5% NaCl. In the present work the study of this composition was continued not only by electrochemical method (taking polarization curves), but also in corrosion tests.

Figure 4 shows the anodic polarization curves of the MNZn5-1 alloy in a borate buffer solution of pH 7.4 containing 0.01 mol/L NaCl and different concentrations of SKAP-25 + SMBT mixture (7.1:1). If we compare this mixture with its main substance, we can see that much lower C_{in} is needed to reduce the i_p of the second peak. Thus, as early as 0.0015 g/L SKAP-25+SMBT suppresses anodic dissolution in the region of the first peak potentials and increases E_{pt} by 0.03 V. With further increase in C_{in} the second peak of anodic dissolution is suppressed and E_{pt} increases up to 1.02 V at $C_{in} = 0.0769 \text{ g/L}$.

Analyzing the results of electrochemical studies, it can be noted that there is a mutual strengthening of protective properties between SKAP-25 and SMBT in their mixture. It is of interest to evaluate the protective capacity of SKAP-25, as well as its composition with SMBT in relation to copper and alloy MNZn5-1 in corrosion tests in an aqueous solution of

chlorides. These tests were carried out on plates of copper and alloy in 0.01 M and 3.5% aqueous solution of NaCl.

Figure 4. Anodic polarization curves of MNZh5-1 alloy in borate buffer solution pH 7.4 containing 0.01 M NaCl (1) with addition of SKAP-25+SMBT mixture (7:1) (in g/L): 2 – 0.012, 3 – 0.025, 4 – 0.046, 5 – 0.077.

Consider the inhibitory properties of dicarboxylate additives for copper protection in a solution containing 0.01 M NaCl (Figure 5a). Already with the introduction of SKAP-25 in an amount of 0.0337 g/L the protective effect $Z = 58\%$ is observed and increases with increasing C_{in} to 0.674 g/L, reaching 100%. Using SMBT, 0.283 g/L CI is required to achieve complete copper protection. Using SKAP-25+SMBT as the CI mixture, at $C_{in} = 0.1537$ g/L the protective effect reaches 98.3%, and fully protects copper at $C_{in} = 0.461$ g/L, which contains 0.057 g/L SMBT, which is almost 5 times less than using SMBT itself. Thus, smaller amounts of SMBT can be used to protect copper by diluting it with SKAP-25. This avoids the substantial alkalization of the medium that occurs when using SMBT itself: the pH of the solution containing 0.1 g/L of this CI is 9.5.

Since the composition of SKAP-25 with SMBT provided high protection of copper against corrosion in 0.01 M NaCl, tests were continued in a more aggressive aqueous solution containing 3.5% NaCl (Figure 5b). Under these conditions at 0.506 g/L SKAP-25 $Z = 40\%$ and increases to 55% at $C_{in} = 1.685$ g/L. Under such severe conditions full protection of copper was achieved only by introduction of SKAP-25+SMBT (7.1:1) at $C_{in} = 1.537$ g/L.

Figure 5. Dependence of the degree of protection of copper in 0.01 M (a) NaCl and 3.5% NaCl solution (b) on the concentration of sodium salts of KAP-25 (curve 2), 2-MBT (curve 1) and their mixture (curve 3).

In the case of the MNZh5-1 alloy in a 0.01 M solution (Figure 6a), the use of SKAP-25 provides $Z=74\%$ at $C_{in}=0.169$ g/L and increases to 87% at $C_{in}=1.011$ g/L. When a mixture of SKAP-25+SMBT (7.1:1) is used, a higher protection efficiency is observed. Already at $C_{in}=0.30$ g/L $Z>95\%$, and at $C_{in}=0.6$ g/L full protection of the alloy is achieved.

Figure 6. Dependence of the degree of protection of MNZh5-1 alloy in 0.01 M (a) NaCl and 3.5% NaCl solution (b) on the concentration of sodium salts of KAP-25 (curve 2), 2-MBT (curve 1) and their mixture (curve 3).

In a more aggressive solution of 3.5% NaCl (Figure 6b) full protection of the alloy is observed only when using SMBT with $C_{in}=0.567$ g/L. SKAP-25 itself is little effective in this solution: even at $C_{in}=1.685$ g/L, $Z=62\%$, but using the composition SKAP-25 + SMBT (7.1:1), it was possible to significantly increase Z to 94.5% .

Conclusions

1. Adsorption of sodium salts of itaconic and succinic acids and, probably, its mixture of alkenyl derivatives SKAP-25 on the oxidized surface of copper and alloy MNZh5-1 in borate buffer solution is of chemical nature.
2. SKAP-25 anions and its composition with SMBT can passivate copper and its alloy MNZh5-1 in borate buffer containing 0.01 M NaCl and prevent their local depassivation by chlorides up to the potentials of oxygen release on the electrode.
3. Corrosion tests of copper and alloy in 0.01 M NaCl and 3.5% NaCl solutions showed that it is possible to increase the protective properties of SKAP-25 using it in the composition with SMBT (at their ratio of 7.1:1). Although it lacks synergistic protective action, it is capable of suppressing copper corrosion without significantly increasing the pH of the solution at $C_{in}=0.461$ g/L in 0.01 M NaCl and 1.537 g/L in 3.5% NaCl. This mixed CI is capable of completely suppressing corrosion of the alloy MNZh5-1 in 0.01 M NaCl solution at $C_{in}=0.6$ g/L and providing a high degree of corrosion protection ($Z=94.5\%$) in 3.5% NaCl at $C_{in}=1.685$ g/L.

References

1. N. Kovačević, I. Milošev and A. Kokalj, How relevant is the adsorption bonding of imidazoles and triazoles for their corrosion inhibition of copper, *Corros. Sci.*, 2017, **124**, 25–34. doi: [10.1016/j.corsci.2017.04.021](https://doi.org/10.1016/j.corsci.2017.04.021)
2. N.K. Allam, A.A. Nazeer and E.A. Ashour, A review of the effects of benzotriazole on the corrosion of copper and copper alloys in clean and polluted environments, *J. Appl. Electrochem.*, 2009, **39**, 961–969. doi: [10.1007/s10800-009-9779-4](https://doi.org/10.1007/s10800-009-9779-4)
3. M. Finšgar and I. Milošev, Inhibition of copper corrosion by 1,2,3-benzotriazole: A review, *Corros. Sci.*, 2010, **52**, 2737–2749. doi: [10.1016/j.corsci.2010.05.002](https://doi.org/10.1016/j.corsci.2010.05.002)
4. M. Petrović Mihajlović and M.M. Antonijević, Copper Corrosion Inhibitors. Period 2008–2014. A Review, *Int. J. Electrochem. Sci.*, 2015, **10**, 1027–1053.
5. S.M. Milić, M.M. Antonijević and M.B. Petrović, Films formed on copper surface in chloride media in the presence of azoles, *Corros. Sci.*, 2009, **51**, 1228–1237. doi: [10.1016/j.corsci.2009.03.026](https://doi.org/10.1016/j.corsci.2009.03.026)
6. Yu.I. Kuznetsov, Triazoles as a class of multifunctional corrosion inhibitors. A review. Part I. 1,2,3-Benzotriazole and its derivatives. Copper, zinc and their alloys, *Int. J. Corros. Scale Inhib.*, 2018, **7**, no. 3, 271–307. doi: [10.17675/2305-6894-2018-7-3-1](https://doi.org/10.17675/2305-6894-2018-7-3-1)
7. H. Huang, Z. Wang, Y. Gong, F. Gao, Z. Luo, S. Zhang and H. Li, Water soluble corrosion inhibitors for copper in 3.5wt% sodium chloride solution, *Corros. Sci.*, 2017, **123**, 339–350. doi: [10.1016/j.corsci.2017.05.009](https://doi.org/10.1016/j.corsci.2017.05.009)
8. H. Otmacic Curkovic, E. Stupnisek-Lisac and H. Takenouti, The influence of pH value on the efficiency of imidazole based corrosion inhibitors of copper, *Corros. Sci.*, 2010, **52**, no. 2, 398–405. doi: [10.1016/j.corsci.2009.09.026](https://doi.org/10.1016/j.corsci.2009.09.026)

-
9. E. Rocca, G. Bertrand, C. Rapin and J.C. Labrune, Inhibition of copper aqueous corrosion by non-toxic linear sodium heptanoate: mechanism and ECAFM study, *J. Electroanal. Chem.*, 2001, **503**, 133–140. doi: [10.1016/S0022-0728\(01\)00384-9](https://doi.org/10.1016/S0022-0728(01)00384-9)
 10. M. Ohsawa and W. Suetaka, Spectro-electrochemical studies of the corrosion inhibition of copper by mercaptobenzothiazole, *Corros. Sci.*, 1979, **19**, no. 10, 709–722. doi: [10.1016/S0010-938X\(79\)80069-4](https://doi.org/10.1016/S0010-938X(79)80069-4)
 11. G. Rajkumar and M.G. Sethuraman, Corrosion protection ability of self-assembled monolayer of 3-amino-5-mercapto-1,2,4-triazole on copper electrode, *Thin Solid Films*, 2014, **562**, 32–36. doi: [10.1016/j.tsf.2014.03.074](https://doi.org/10.1016/j.tsf.2014.03.074)
 12. G. Chan-Rosado and M.A. Pech-Canul, Influence of native oxide film age on the passivation of carbon steel in neutral aqueous solutions with a dicarboxylic acid, *Corros. Sci.*, 2019, **153**, 19–31. doi: [10.1016/j.corsci.2019.03.033](https://doi.org/10.1016/j.corsci.2019.03.033)
 13. F. Capriolim, A. Martinellim, V. DiCastrom and F. Decker, Effect of various terminal groups on long-term protective properties of aromatic SAMs on copper in acidic environment, *J. Electroanal. Chem.*, 2013, **693**, 86–94. doi: [10.1016/j.jelechem.2013.01.025](https://doi.org/10.1016/j.jelechem.2013.01.025)
 14. M.O. Agafonkina, Yu.I. Kuznetsov and N.P. Andreeva, Inhibitor Properties of Carboxylates and Their Adsorption on Copper from Aqueous Solutions, *Russ. J. Phys. Chem. A*, 2015, **89**, no. 6, 1070–1076. doi: [10.1134/S0036024415060023](https://doi.org/10.1134/S0036024415060023)
 15. E. Abelev, D. Starosvetsky and Y. Ein-Eli, Enhanced Copper Surface Protection in Aqueous Solutions Containing Short-Chain Alkanoic Acid Potassium Salts, *Langmuir*, 2007, **23**, 11281–11288. doi: [10.1021/la701434e](https://doi.org/10.1021/la701434e)
 16. G.T. Hefter, N.A. North and S.H. Tan, Organic corrosion inhibitors in neutral solutions. Part 1. Inhibition of steel, copper and aluminum by straight chain carboxylates, *Corrosion*, 1997, **53**, 657–667. doi: [10.5006/1.3290298](https://doi.org/10.5006/1.3290298)
 17. K. Aramaki and T. Shimura, Self-assembled monolayers of carboxylate ions on passivated iron for preventing passive film breakdown, *Corros. Sci.*, 2004, **46**, 313–328. doi: [10.1016/S0010-938X\(03\)00156-2](https://doi.org/10.1016/S0010-938X(03)00156-2)
 18. U. Rammelt, S. Köhler and G. Reinhard, Electrochemical characterization of the ability of dicarboxylic acid salts to the corrosion inhibition of mild steel in aqueous solutions, *Corros. Sci.*, 2011, **53**, 3515–3520. doi: [10.1016/j.corsci.2011.06.023](https://doi.org/10.1016/j.corsci.2011.06.023)
 19. D. Lahem, M. Poelman, F. Atmani and M.G. Olivier, Synergistic improvement of inhibitive activity of dicarboxylates in preventing mild steel corrosion in neutral aqueous solutions, *Corros. Eng., Sci. Technol.*, 2012, **47**, 463–471. doi: [10.1179/1743278212Y.0000000030](https://doi.org/10.1179/1743278212Y.0000000030)
 20. G. Chan-Rosado and M.A. Pech-Canul, Influence of native oxide film age on the passivation of carbon steel in neutral aqueous solutions with a dicarboxylic acid, *Corros. Sci.*, 2019, **153**, 19–31. doi: [10.1016/j.corsci.2019.03.033](https://doi.org/10.1016/j.corsci.2019.03.033)
 21. G. Žerjav and I. Milošev, Carboxylic Acids as Corrosion Inhibitors for Cu, Zn and Brasses in Simulated Urban Rain, *Int. J. Electrochem. Sci.*, 2014, no. 9, 2696–2715.

-
22. A.D. Mercer, The properties of carboxilates as corrosion inhibitors for steel and other metals in neutral aqueous solutions, *In Proceeding of the 5th Europ. Symp. on Corros. Inhib.*, Ferrara (Italy), 1980, **2**, 563–581.
 23. Yu.I. Kuznetsov, I.A. Kuznetsov and D.B. Vershok, Copper corrosion protection in neutral media by dicarboxylic acid salts, *Int. J. Corros. Scale Inhib.*, 2019, **8**, no. 4, 1022–1034. doi: [10.17675/2305-6894-2019-8-4-13](https://doi.org/10.17675/2305-6894-2019-8-4-13)
 24. TU 2499-080-05015207-2003, *An additive to anticorrosion formulations to prevent rusting of metal surfaces* (in Russian).
 25. GOST 492–2006, Nickel, nickel and copper-nickel mechanically worked alloys. Brands (in Russian).
 26. R.M. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light*, North-Holland, Amsterdam, 1977, 529 p.
 27. P. Silva-Bermudez, S.E. Rodil and S. Muhl, Albumin adsorption on oxide thin films studied by spectroscopic ellipsometry, *Appl. Surf. Sci.*, 2011, **258**, 1711–1718. doi: [10.1016/j.apsusc.2011.10.020](https://doi.org/10.1016/j.apsusc.2011.10.020)
 28. L. Wang, C. Zhao, M.H.G. Duits, F. Mugele and I. Siretanu, Detection of ion adsorption at solid–liquid interfaces using internal reflection ellipsometry, *Sens. Actuators, B*, 2015, **210**, 649–655. doi: [10.1016/j.snb.2014.12.127](https://doi.org/10.1016/j.snb.2014.12.127)
 29. M.O. Agafonkina, N.P. Andreeva, Yu.I. Kuznetsov and S.F. Timashev, Substituted Benzotriazoles as Inhibitors of Copper Corrosion in Borate Buffer Solutions, *Russ. J. Phys. Chem. A*, 2017, **91**, no. 8, 1414–1421. doi: [10.1134/S0036024417080027](https://doi.org/10.1134/S0036024417080027)
 30. M.O. Agafonkina, I.A. Kuznetsov, N.P. Andreeva and Yu.I. Kuznetsov, Copper protection with sodium salts of lower dicarboxylic acids in neutral aqueous solution, *Int. J. Corros. Scale Inhib.*, 2020, **9**, no. 3, 1000–1013. doi: [10.17675/2305-6894-2020-9-3-13](https://doi.org/10.17675/2305-6894-2020-9-3-13)
 31. M.O. Agafonkina, I.A. Kuznetsov, Yu.I. Kuznetsov, O.Yu. Grafov and N.P. Andreeva, Corrosion inhibition of MNZh alloy with sodium salts of lower dicarboxylic acids in neutral aqueous solution, *Int. J. Corros. Scale Inhib.*, 2021, **10**, no. 1, 349–367. doi: [10.17675/2305-6894-2020-10-1-20](https://doi.org/10.17675/2305-6894-2020-10-1-20)