

# Inhibition of anodic dissolution and corrosion of copper and its alloy in aqueous solutions by fuchsin

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## Abstract

The adsorption of acid fuchsin (AF) and its inhibiting properties toward the anodic dissolution and corrosion of copper alloy MNZh5-1 and its components (Cu, low-carbon steel St3, Ni) were studied in neutral and alkaline solutions. The adsorption of AF on the alloy and copper in a neutral medium proceeds better than in a weakly alkaline medium. On the oxidized surface of St3 in an environment with pH 9.2, adsorption occurs in the region of lower concentrations than at pH 7.4. The adsorption of AF in a neutral solution on Cu and MNZh5-1 alloy free from oxides is described by the complete Temkin equation with the free energy of adsorption ( $-\Delta G_{a, \max}^0$ ) = 47.2 and 80.2 kJ/mol, respectively. This is significantly higher than in a slightly alkaline environment where ( $-\Delta G_{a, \max}^0$ ) = 37.3 and 55.8 kJ/mol, respectively. The orientation of AF on the oxidized surface of copper and the alloy is close to vertical. Corrosion tests of copper in 0.01 M NaCl solution showed that addition of 1.5 mmol/L AF completely suppressed copper corrosion. On the MNZh5-1 alloy under the same conditions, the degree of protection is  $Z = 49.3\%$ . In 3.5% NaCl solution at  $C_{\text{inh}} = 1.0$  mmol/L, the degree of copper protection reaches 60.5%, while that of the alloy is 22%.

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## Introduction

Chemical compounds of the triphenylmethane series are used as synthetic dyes for a wide range of applications (fabric, paper, ink, pencils) [1, 2] and as antimicrobial agents in medicine [3]. This area of their application has determined the production in industry and the economic availability of some of them. In this regard, it is not surprising that there is interest in such substances as possible corrosion inhibitors (CIs) of metals in a wide pH range.

There are many works in the literature in which dyes are considered as CI of ferrous and non-ferrous metals in acidic solutions. For example, back in the early 1980s [4], the inhibition of corrosion of an aluminum-copper alloy in solutions of 0.5 M HCl by

triphenylmethane, anthraquinone and acridine dyes was studied. The dependences on the concentration of acid and CI, the duration of immersion and temperature were obtained. In general, at a constant acid concentration, the effectiveness of malachite green, methyl violet and light green in this function increases, while the effectiveness of basic fuchsin and crystal violet decreases with increasing concentration of CI ( $C_{inh}$ ). The efficiency of all studied CIs increases with increasing temperature ( $t$ ) from 20° to 50°C. At  $C_{inh}=0.1\%$  in 0.5 M HCl, it grows in the following order: fuchsine acid (32%) < fuchsine base (39%) < alizarin red S (46%) < methyl violet 6B (50%) < malachite green (64%) < crystal violet (70%) < light green (80%).

Later, triphenylmethane dyes (AF and BF) were studied on copper in solutions of citric acid [5] and hydrochloric acid at  $C_{inh}=0.001$  M, 0.005 M, and 0.01 M [6]. According to the results of corrosion tests using the gravimetric method, the order of effectiveness of copper protection in solutions of both acids is as follows: BF=1,2,3-benzotriazole > AF. The resulting adsorption isotherms correspond to the Frumkin isotherm model. A thermodynamic/kinetic model of adsorption was established and the orientation of the CI molecule was identified based on its area size during the adsorption process. The area occupied by vertically oriented AF molecules is 83.56 A<sup>2</sup>, the area of horizontal orientation is 113.85 A<sup>2</sup>, and the area occupied by a vertically adsorbed water molecule is in the range from 8 to 12 A<sup>2</sup>. Calculations using the ViewerPro program from Molecular Simulation Inc. showed that the experimental data can be interpreted as vertical adsorption of AF on the copper surface.

A fuchsin derivative, New Fuchsin, was studied on low-carbon steel in a 1 M HCl solution using electrochemical noise measurements and electrochemical impedance spectroscopy (EIS) [7]. According to the results obtained, New Fuchsin is an effective CI even at  $C_{inh}=5$  mg/L. EIS studies have shown that the polarization resistance of steel in 1 M HCl increases with increasing  $C_{inh}$ .

Studies of AF on steel in solutions of 2 M acids (H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl) were carried out in [8–11]. Ya.G. Avdeev *et al.* [8], using X-Ray photoelectron spectroscopy to analyze the surface of steel after keeping it in a 2 M solution of these acids, came to the conclusion that the protection against corrosion of AF is due to the formation of its polymer complex with metal cations. In HCl solution, the protective layer consists of an iron oxide/hydroxide mixture directly bonded to the metal. On top of this layer is a chemisorbed polymer complex of triphenylmethane molecules and Fe(II) cations. At the boundary with the solution there are CI layers connected to each other and to the underlying layer of the polymer complex by physical forces. In solutions of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, the protective layer mainly consists of a polymer complex chemically bound to the steel surface (or a mixture of iron oxides and hydroxides covering it), formed by triphenylmethane molecules, thiocyanate anions and Fe(II) cations.

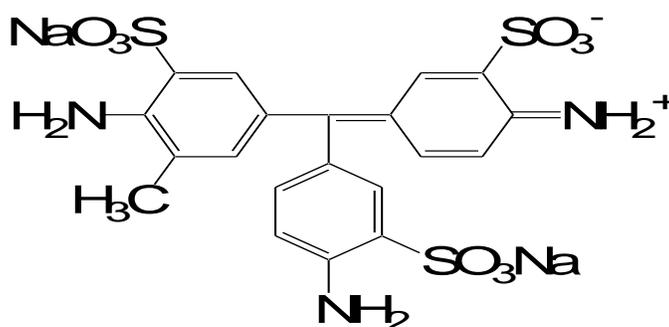
When studying the corrosion of St3 steel in a 2 M solution of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, AF and brilliant green, which contain a conjugated triphenylmethane ring, have a high protective effect [10]. To protect St3 steel in solutions of mineral acids 2 M H<sub>2</sub>SO<sub>4</sub>, HCl and H<sub>3</sub>PO<sub>4</sub> in

a wide temperature range,  $t=25-95^{\circ}\text{C}$ , the authors recommend compositions of AF with IFKhAN-92, catamine AB (in HCl solution), potassium thiocyanate KNCS (in  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ ). These mixtures effectively inhibit the electrode reactions on St3 steel in acidic environments.

AF is well known as the CI of low-carbon steel St3 in acidic environments, but it has been little studied as an CI of metals in neutral environments. The aim of this study is to identify the patterns of adsorption, passivation and protective properties of AF from neutral (pH 7.4) and weakly alkaline (pH 9.2) solutions on the MNZh5-1 alloy and on the components of its components: copper, nickel and iron (St3).

## Experimental

Studies of the inhibitory effect and adsorption of commercial AF –  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{Na}_2\text{O}_9\text{S}_3$ ,  $M_r=585.5$  g/mol (the structural formula of AF is shown in Figure 1), were carried out on copper alloy MNZh5-1 whose composition is presented in Table 1 [12], copper M1 (99.9% Cu), nickel N0, and low-carbon steel grade steel St3 [13]. A concentrated solution of 0.02 M AF was prepared in borate buffer solutions with pH 7.4 and 9.2.



**Figure 1.** Structural formula of acid fuchsin

**Table 1.** Chemical composition of the MNZH 5-1 material (%)

Ni+Co	Fe	C	Si	S	P	Cu	Zn	Sb	Sn
5.0–6.5	1–1.4	<0.03	<0.15	<0.01	<0.04	90.6–93.7	<0.5	<0.005	<0.1

Electrochemical studies consisted of recording polarization curves in a borate buffer solution with pH 7.4 or 9.2 with the addition of 0.01 M NaCl. Polarization measurements on the metals under study were carried out in borate buffer solutions with pH 7.4 or 9.2 containing 0.01 M NaCl. Anodic polarization curves were recorded using an IPC-PRO potentiostat<sup>1</sup> on an electrode made of M1 copper (surface area  $S=0.785$  cm<sup>2</sup>), MNZh5-1

<sup>1</sup> The cathodic polarization curves of St3 steel were measured in a chloride-buffer solution with pH 7.4 and pH 9.2. All operations were carried out sequentially, similarly to recording the anodic polarization curves but with an opposite (negative) direction of the potential sweep, at a speed of 0.2 mV/s.

alloy ( $S=0.5 \text{ cm}^2$ ) and St3 steel ( $S=0.785 \text{ cm}^2$ ) in an electrochemical cell with separated electrode spaces. The working electrode was preliminarily polished on emery papers of various grain sizes 360–1000 and then degreased with acetone. The potentials  $E$  of the electrode in solution were measured relative to the silver chloride reference electrode, and their values in the article are given in terms of the standard hydrogen scale. The auxiliary electrode was made of pyrographite.

The air-formed oxide on Cu and MNZh5-1 alloy was removed by keeping the electrode for 15 min in a borate buffer (pH 9.2) with 0.01 M NaCl at  $E=-0.6 \text{ V}$ , and on St3 steel at  $E=-0.65 \text{ V}$ . Then the potentiostat was turned off until the free corrosion potential  $E_{\text{cor}}$  was established. After a new  $E_{\text{cor}}$  value established after AF added to the buffer solution adsorbed on the electrode, polarization curves were recorded at a potential sweep rate of 0.2 mV/s. The potential of local depassivation of metal by chlorides ( $E_{\text{ld}}$ ) was determined from a sharp increase in current on the polarization curve, followed by visual identification of pits on the electrode surface. The  $E_{\text{ld}}$  measurement error is 0.01 V. The ability of the CI to prevent local depassivation was determined as the difference between  $E_{\text{ld}}^{\text{inh}}$  in a solution with AF and in the original borate buffer  $E_{\text{ld}}^{\text{backg}}$  containing 0.01 mol/L NaCl:  $\Delta E = E_{\text{ld}}^{\text{inh}} - E_{\text{ld}}^{\text{backg}}$ .

AF adsorption was measured by the *in situ* ellipsometry method [14]. The studies were carried out with a manually operated ellipsometer RR 2000 in an electrochemical cell. This made it possible to maintain the electrode potential using an IPC-PRO potentiostat and simultaneously measure the ellipsometric angles ( $\Delta$  and  $\Psi$ ) [14]. The accuracy in determining the phase shift angle is  $\pm 0.05^\circ$ . At thicknesses  $d \leq 10 \text{ nm}$  of a homogeneous film, a relationship between its thickness  $d$  and the changes in the  $\Delta$  angle exists:

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

where  $\alpha$  is the proportionality coefficient,  $\Delta_0$  is the angle value for the original surface, and  $\Delta$  is the angle value measured in the experiment.

To obtain an adsorption isotherm, an AF concentrate was added in portions to a cell with a borate buffer solution. For each  $C_{\text{inh}}$ , the angle  $\Delta$  decreases with time and stops changing after 60–90 minutes. With a growth of the film, the  $\Delta$  angle decreases, the difference  $(\Delta - \Delta_0)$  is  $< 0$ , and the angle  $\Delta = -\alpha\delta\Delta = -\alpha(\Delta - \Delta_0)$  increases upon dissolution; that is, the difference  $(\Delta - \Delta_0)$  is  $> 0$ . Thus, the difference of angles ( $-\delta\Delta$ ) is determined to plot the dependence on  $C_{\text{inh}}$  for AF. The value of  $C_{\text{inh}}$ , at which the angle  $\Delta$  does not change, corresponds to the formation of a conditional monolayer and the degree of coverage of the electrode surface by the adsorbate  $\Theta \rightarrow 1$ . The experimental dependence of  $(-\delta\Delta)$  on  $\log C_{\text{inh}}$  is converted to the adsorption isotherm  $\Theta = f(\log C)$  and is determined by the equation, using which the free energy of adsorption of AF ( $-\Delta G_a^0$ ) can be evaluated. In the case considered, the adsorption of AF is adequately described by the full Temkin equation [15]:

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

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

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

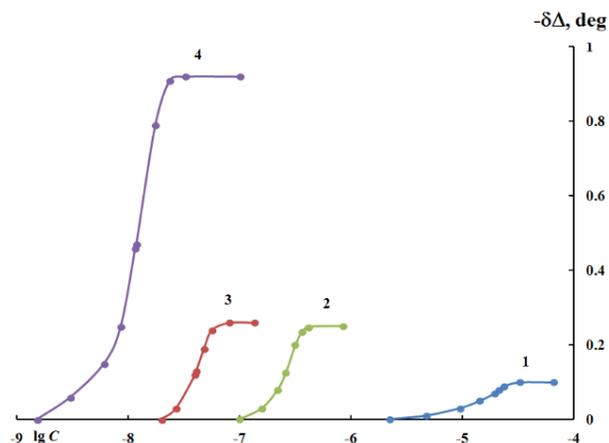
To determine ( $-\Delta G_a^0$ ), ( $-\Delta G_{a, \min}^0$ ),  $f$  factor,  $B_{\max}$ , and  $B_{\min}$ , we used the technique described previously [15].

Corrosion tests of copper and copper alloy were carried out in distilled water containing 0.01 M NaCl and various AF concentrations. Before the experiment, metal plates were cleaned on abrasive paper of different grit (from P360 to P1000), degreased with acetone and weighed. The weighing error was 0.0002 g. Then the samples were placed in a chloride solution containing various AF concentrations were kept at room temperature  $t = (22 \pm 2)^\circ\text{C}$  and with natural aeration. After 7 days, the plates were removed, cleaned from corrosion products, and weighed again. Based on the difference in sample masses before and after a tests, the corrosion rates in the background ( $K_0$ ) and inhibited solution ( $K_{\text{inh}}$ ) were calculated and the degree of metal protection  $Z$  was determined using the formula:

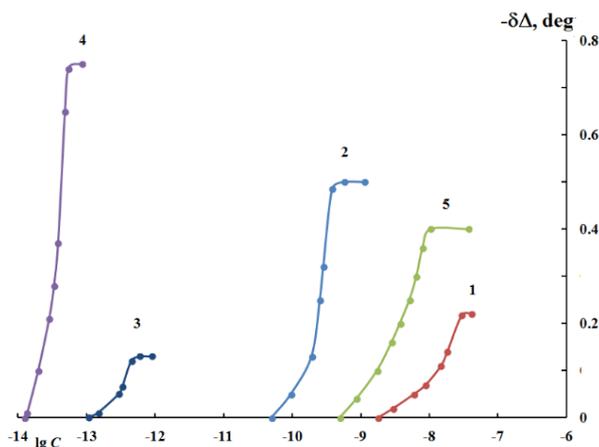
$$Z = \frac{K_0 - K_{\text{inh}}}{K_0} \cdot 100\% \quad (4)$$

## Results and Discussion

We studied the passivation and adsorption properties of AF in a neutral borate buffer containing 0.01 M NaCl on copper and the MNZh5-1 alloy previously [16]. It was shown that the transition from copper to alloy MNZh5-1 significantly facilitated the adsorption of AF in the neutral environment. To measure the adsorption isotherm of AF on the oxidized copper and the alloy in the alkaline environment, adsorption measurements were carried out at  $E=0.0$  V (Figure 2). According to the Pourbaix diagram [17] for the Cu–H<sub>2</sub>O system, this potential corresponds to the oxidation of copper and the coating of its surface with Cu(II) oxide.



**Figure 2.** Plots of  $(-\delta\Delta)$  vs.  $\lg C$  of AF on reduced surface of the copper at  $E=-0.6$  V, pH 9.2 (1) and pH 7.4 (2), and on oxidized surface of copper at  $E=0.0$  V, pH 9.2 (3) and pH 7.4 (4).



**Figure 3.** Plots of  $(-\delta\Delta)$  vs.  $\lg C$  of AF on reduced surface of MNZn5-1 alloy at  $E=-0.6$  V, pH 9.2 (1) and pH 7.4 (3), and on oxidized surface of the copper alloy at  $E=0.0$  V, pH 9.2 (2) and pH 7.4 (4), on oxidized surface of nickel at  $E=0.2$  V, pH 7.4 (5).

In an alkaline environment, the adsorption of AF on the alloy surface begins at lower  $C_{\text{inh}}$  compared to adsorption on copper. The corresponding adsorption isotherms of AF on the oxidized and reduced surface of the alloy and copper in environments with pH 7.4 and 9.2 are shown in Figures 2 and 3. Examination of these figures clearly shows that an increase in the solution alkalinity worsens the adsorption of AF on copper and on the alloy. Their adsorption isotherms begin at higher  $C_{\text{inh}}$  than in neutral solutions.

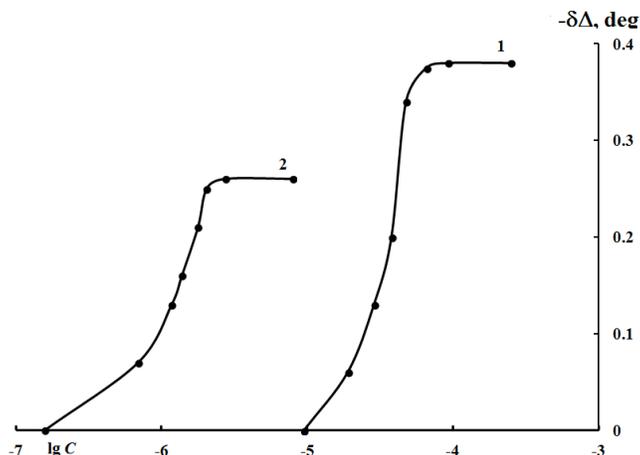
Table 2 shows the adsorption constants for copper and its alloy in these environments. The highest adsorption energy of AF on an oxidized alloy in a neutral environment is  $(-\Delta G_{\text{a,max}}^0)=86.3$  kJ/mol. The deterioration of AF adsorption on the alloy with increasing alkalinity of the environment can be explained by deprotonation of the AF molecule upon transition from a neutral to a weakly alkaline environment (Figure 1). Thus a negative charge only remains on the  $\text{SO}_3$  group, which probably leads to weakening of the bond with the surface of the oxidized hydrated metal.

**Table 2.** Characteristics of the adsorption of AF on the surface of metals with different pH values: minimum and maximum values of  $B$ ,  $(-\Delta G_{a, \max}^0)$ ,  $(-\Delta G_{a, \min}^0)$ , and the  $f$  coefficient.

Metal and its potential, $E$ , V	pH	$B_{i, \max}$ , L/mol	$B_{i, \min}$ , L/mol	$(-\Delta G_{a, \min}^0)$ , kJ/mol	$(-\Delta G_{a, \max}^0)$ , kJ/mol	$f$
Copper, $-0.6$ V	7.4	$3.3 \cdot 10^6$	$1.1 \cdot 10^6$	44.4	47.2	1.10
Copper, $0.0$ V	7.4	$9.3 \cdot 10^9$	$1.7 \cdot 10^9$	52.6	55.4	1.28
Copper, $-0.6$ V	9.2	$6.3 \cdot 10^4$	$2.1 \cdot 10^4$	34.7	37.3	1.06
Copper, $0.0$ V	9.2	$2.2 \cdot 10^7$	$1.1 \cdot 10^7$	49.9	51.8	0.66
MNZh5-1, $-0.6$ V	7.4	$2.1 \cdot 10^{12}$	$8.8 \cdot 10^{11}$	78.1	80.2	0.83
MNZh5-1, $0.0$ V	7.4	$4.6 \cdot 10^{14}$	$2.4 \cdot 10^{13}$	83.6	86.3	1.11
MNZh5-1, $-0.6$ V	9.2	$1.1 \cdot 10^8$	$4.6 \cdot 10^7$	53.6	55.8	0.87
MNZh5-1, $0.0$ V	9.2	$3.6 \cdot 10^9$	$1.1 \cdot 10^9$	61.6	64.5	1.17
St 3, $0.2$ V	7.4	$2.4 \cdot 10^4$	$9.2 \cdot 10^3$	32.5	34.9	0.97
	9.2	$1.1 \cdot 10^6$	$1.7 \cdot 10^5$	39.7	44.4	1.91
Ni, $0.2$ V	7.4	$6.3 \cdot 10^8$	$7.7 \cdot 10^7$	54.9	60.1	2.1

From comparison of  $(-\delta\Delta)$  variation that is proportional to the thickness  $\delta$  of the adsorbed layer on the oxidized and reduced surface of copper and its alloy, we can conclude that the orientation of AF on the oxidized surface of copper and MNZh5-1 alloy is close to vertical. It is also consistent with the conclusions of the authors [8] who examined the inhibition of copper corrosion with AF in 0.001–0.01 M HCl solutions. The high adsorption activity of MNZh5-1 alloy may be associated, to a great extent, with the nickel content in the range of 5–6 wt.%) (Table 1). Adsorption on nickel oxidized at  $E=0.2$  V (Figure 3, isotherm 5) in the concentration area  $\lg C=-9.30\dots-7.40$  occurs with  $(-\Delta G_{a, \max}^0)=60.1$  kJ/mol. The adsorption of AF on other alloy components is significantly weaker: on copper  $(-\Delta G_{a, \max}^0)=55.4$  kJ/mol and on St3 steel,  $(-\Delta G_{a, \max}^0)=34.95$  kJ/mol.

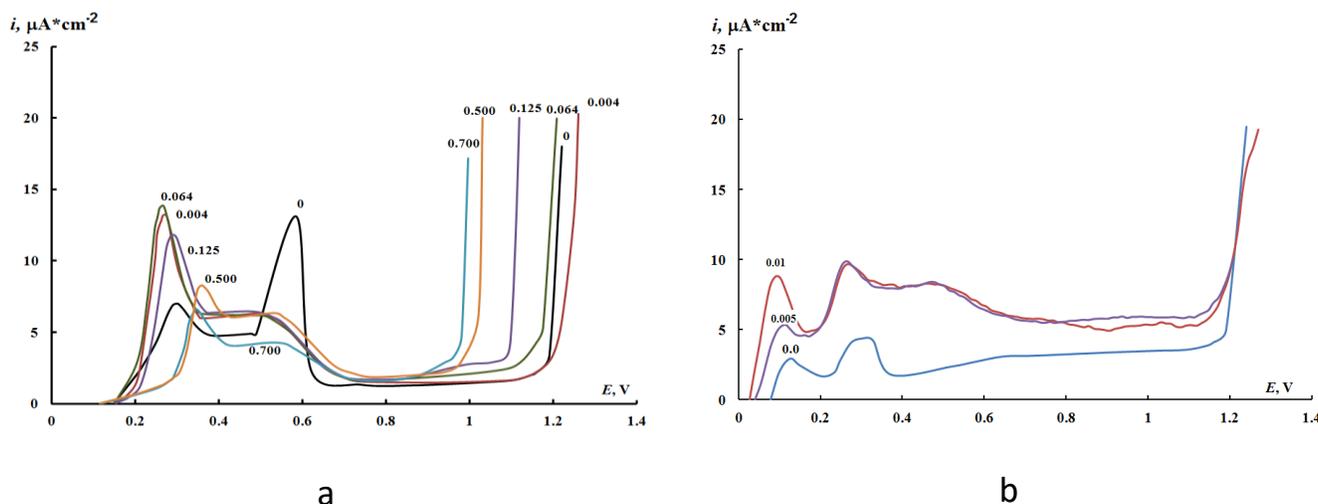
The plots of AF adsorption on a pre-oxidized surface of St3 steel in a neutral and alkaline buffer solutions are presented in Figure 4. From the figure it follows that in the slightly alkaline environment, the adsorption of AF begins at  $C_{\text{inh}}$  that is smaller by 2 orders:  $0.12 \mu\text{mol/L}$  (pH 9.2) and  $10 \mu\text{mol/L}$  (pH 7.4). In a neutral buffer solution  $(-\Delta G_{a, \max}^0)=34.95$  kJ/mol, which apparently testifies to the physical adsorption of AF on oxidized steel. With an increase in the pH of the medium, the chemical interaction of AF with oxidized steel is more likely, in this case  $(-\Delta G_{a, \max}^0)=44.4$  kJ/mol (Table 2).



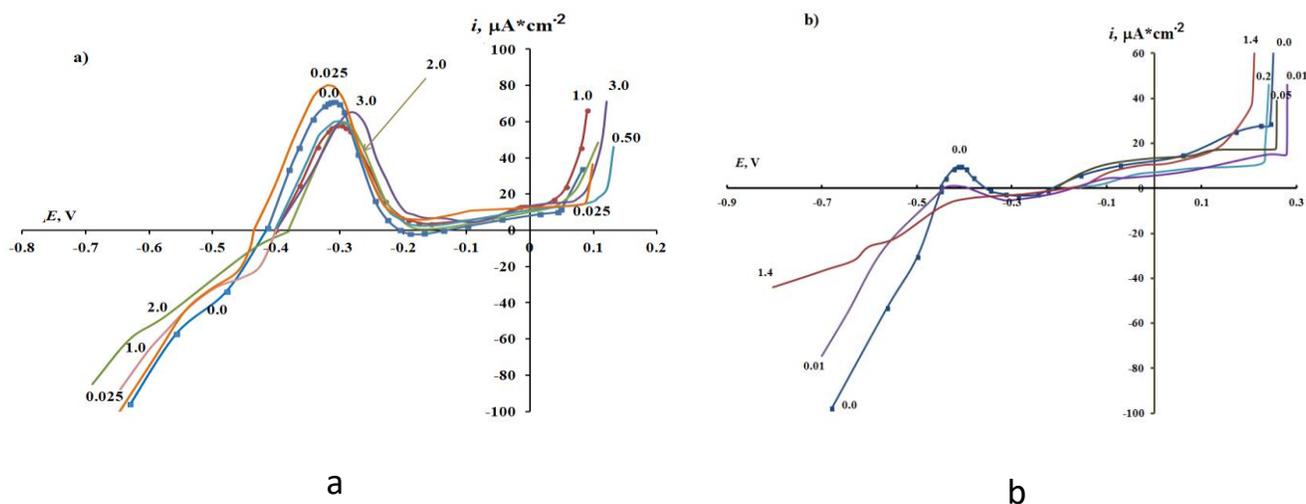
**Figure 4.** Plot of  $(-\delta\Delta)$  on  $\lg C$  of AF on St3 steel surface pre-oxidized at  $E=0.2$  V in borate buffer solutions with pH 7.4 (1) and pH 9.2 (2)

The differences in the adsorption of AF on the alloy, copper and St3 steel can also be traced on the anodic polarization curves. It has been shown [16] that in a neutral environment, anodic polarization curves of Cu and its alloy have two peaks of anodic dissolution. On a Cu electrode, AF in the entire studied  $C_{inh}$  range is not able to suppress the second peak of anodic current density (at  $E=0.30$  V). With an increase in the added AF concentration  $C_{inh}$  from 0.04 to 0.85 mmol/L,  $E_{ld}$  grows and the protective effect  $\Delta E$  reaches 0.18 V. As the concentration reaches  $C_{inh}=0.85$  mmol/L, the current density in the second peak increases to  $68 \mu\text{A}/\text{cm}^2$ . Apparently, at  $C_{inh} \geq 0.85$  mmol/L, soluble complexes of AF with the cation  $\text{Cu}^{2+}$  are formed. On the alloy, AF at  $C_{inh}=0.008$  mmol/L first suppresses the of the first peak of anodic dissolution, and with an increase to  $C_{inh}=0.014$  mmol/L, the second peak as well. Significant inhibition of the alloy depassivation requires the presence of a smaller AF amount than in the case of Cu. With an increase in  $C_{inh}$ ,  $E_{ld}$  shifts to the potentials of oxygen evolution to reach  $\Delta E \sim 0.3$  V at  $C_{inh}=1.0$  mmol/L.

The anodic polarization curves of Cu and the MNZh5-1 alloy in a chloride-buffer solution (pH 9.2) with addition of AF are shown in Figure 5. This alloy is relatively stable in this medium and its  $E_{ld}$  is already in the area of potentials corresponding to the release of oxygen (Figure 5b). On the anodic polarization curve at pH 9.2, two peaks of anodic dissolution of the alloy are also observed, but with  $i_p$  lower than in the neutral environment. Addition of small quantities of AF,  $C_{inh}=0.005$  or 0.01 mmol/L, increases the first peak 1.5- and 2.5-fold, respectively, and the second peak twofold. The values of these peaks are  $\leq 10 \mu\text{A}/\text{cm}^2$ .



**Figure 5.** Anodic polarization curves of copper (a) and MNZh5-1 (b) in a chloride-buffer solution (pH 9.2) with addition of AF. The numbers next to the curves show the  $C_{\text{inh}}$  values (in mmol/L).



**Figure 6.** Anodic and cathodic polarization curves of low-carbon steel St3 in a chloride-buffer solution with addition of AF: a) pH 7.4 and b) pH 9.2. The numbers next to the curves show the  $C_{\text{inh}}$  values (in mmol/L).

As indicated above,  $(-\Delta G_{\text{a,max}}^0)$  AF on steel St3 is minimal compared to the other components of the alloy. Figure 6 presents cathodic polarization curves of St3 in buffer solutions with pH 7.4. Unlike copper and the alloy, on St3 spontaneous passivation of the electrode in a slightly alkaline solution is observed and  $(-\Delta G_{\text{a,max}}^0)$  increases. In this solution,  $i_{\text{p}} \sim 10 \mu\text{A}/\text{cm}^2$ , and even 0.01 mmol/L AF almost spontaneously transfers steel St3 into a passive state without changing  $E_{\text{ld}}$  (Figure 6). With an increase in the AF concentration, a decrease in  $E_{\text{ld}}$  is observed. Probably, in an alkaline environment, soluble complex compounds are formed from surface iron cations and AF anions.

In a neutral solution, in the entire studied range of  $C_{inh}$  (0.05–3.0 mmol/L), AF cannot passivate the steel electrode. At  $C_{inh}=0.025$  mmol/L, the current density of the anodic dissolution of steel,  $i_p$ , increases by  $10 \mu\text{A}/\text{cm}^2$ , while  $E_{ld}$  increases by 0.05 V relative to the background curve. At  $C_{inh}=0.5$  mmol/L, the protective effect  $\Delta E$  reaches 0.08 V. With an increase in  $C_{inh}$  from 0.5 to 3 mmol/L, a slight decrease in  $i_p$  from 70 to  $54 \mu\text{A}/\text{cm}^2$  occurs, but no noticeable  $E_{ld}$  shift is observed.

Cathodic polarization curves on steel St3 in a neutral and slightly alkaline solution show a greater inhibition of this electrode reaction than anode. Here, a decrease in the cathodic reaction rate with an increase in  $C_{inh}$  is observed.

From the above results of adsorption and polarization measurements, we can conclude that changes in the pH of the environment affects the adsorption of AF on low-carbon steel, copper and its alloy MNZn5-1. An increase in the pH of the medium improves the adsorption of AF on steel but, in contrast, hinders it on copper and MNZn5-1 alloy.

The protective ability of AF was determined in corrosion tests on Cu and alloy in 0.01 M aqueous solution of NaCl (Table 3). From the data presented in it, it can be seen that 0.25 mmol/L AF provides the degree of protection  $Z=91.5\%$  and 41% on Cu and MNZn5-1, respectively. In the case of Cu,  $Z$  increases in proportion to the concentration of the solution, reaching complete protection of the metal at  $C_{inh}=1.5$  mmol/L (Table 3), while it decreases with the solution pH. The situation on the alloy is different: with each increase in  $C_{inh}$  by 0.25 mmol/L,  $Z$  of the alloy grows slightly to reach the maximum value  $Z=49.3\%$  at  $C_{inh}=2$  mmol/L.

Under more severe conditions (3.5% sodium chloride solution), the degree of protection is lower than in the 0.01 M solution. In fact, at  $C_{inh}=1.0$  mmol/L AF, the degree of copper protection reaches only 60.5%, while  $Z=22\%$  for the alloy. On the MNZn5-1 alloy, over the entire concentration range studied, no high protection is observed compared to copper, and the degree of protection  $Z$  does not exceed 22%.

**Table 3.** Corrosion tests of copper and MNZn5-1 alloy in 0.01 M NaCl solution for 7 days with natural aeration.

$C$ , mmol/L	Copper $K$ , g/m <sup>2</sup> ·day	Copper $Z$ , %	MNZn5-1 $K$ , g/m <sup>2</sup> ·day	MNZn5-1 $Z$ , %
0	0.870	–	0.73	–
0.25	0.070	91.5	0.43	41
0.50	0.063	92.7	0.40	45.2
0.75	0.040	95.1	0.39	46.5
1.0	0.020	97.7	0.38	47.8
1.5	0.000	100	0.37	49.3

**Table 4.** Corrosion tests of copper and MNZh5-1 alloy in 3.5% NaCl solution for 7 days with natural aeration.

C, mmol/L	pH	Copper Z, %	MNZh5-1 Z, %
0	6.20	–	–
0.25	6.28	2.1	–
0.50	6.13	50.0	15.3
0.75	5.90	55.6	21.1
1.0	5.40	60.5	22
1.5	3.75	63.2	19
2.0	3.62	68.1	17

It seemed that these data contradict with adsorption data, from which it followed that ( $-\Delta G_{a, \max}^0$ ) for the alloy was the largest. The adsorption isotherm was obtained at  $E=0.2$  V, whereas the corrosion tests were carried out at  $E_{\text{cor}}$ . The elemental composition of the surface of the MNZh5-1 alloy determined at  $E_{\text{cor}}$  and at  $E=0.2$  V by XPS [18] shows an enrichment of the surface with iron at  $E_{\text{cor}}$ . For samples exposed at  $E_{\text{cor}}$  the elemental composition was: Cu 88.67%; Ni 5.43%; Fe 5.9%. The composition at  $E=0.2$  V was: Cu 93.57%; Ni 4.22%; Fe 2.21%. The alloy contains 1.0–1.4% Fe according to GOST.

Analyzing the results of elemental analysis and electrochemical studies, we can conclude that the iron component of the alloy MNZh5-1 reduces the resistance to the corrosive effect of chloride ions.

## Conclusions

1. Adsorption of AF on the pre-oxidized surface of Cu or MNZh5-1 alloy at  $E=0.0$  V in a neutral environment with pH 7.4 is described by the complete equation of the Temkin isotherm with the free energy of adsorption ( $-\Delta G_{a, \max}^0$ )=55.4 and 86.3 kJ/mol, respectively. This is significantly higher than in a slightly alkaline environment with pH 9.2 where ( $-\Delta G_{a, \max}^0$ )=51.8 and 64.5 kJ/mol, respectively.
2. On the surfaces of Cu and MNZh5-1 alloy free from oxides, in the neutral solution at  $E=-0.60$  V, the adsorption of AF is also described by the complete Temkin equation with ( $-\Delta G_{a, \max}^0$ )=47.2 and 80.2 kJ/mol, respectively. This is significantly higher than in the slightly alkaline environment where ( $-\Delta G_{a, \max}^0$ )=37.3 and 55.8 kJ/mol, respectively. the orientation of AF on oxidized surfaces of copper and alloy is close to vertical.
3. In the weakly alkaline environment, the MNZh5-1 alloy is relatively stable and its  $E_{\text{ld}}$  is already in the potential region corresponding to the release of  $\text{O}_2$ . Addition of AF to the alkaline medium does not affect  $E_{\text{ld}}$ , but the  $i_p$  of both peaks increases, though their values at the same concentrations is lower than in the neutral medium.

4. On St3 steel, the presence of AF reduces  $i_p$  on the anodic polarization curves in the neutral environment. In the slightly alkaline environment with pH 9.2, AF inhibits anodic dissolution. On low-carbon steel, increasing the pH of the medium improves the adsorption of AF. The values of  $(-\Delta G_{a, \max}^0)$  in the neutral and weakly alkaline borate solutions are 34.9 and 44.4 kJ/mol, respectively. Such values  $(-\Delta G_{a, \max}^0)$  suggest that chemical interaction of AF with the St3 surface occurs in these media, although it is not strong.
5. A high value  $(-\Delta G_{a, \max}^0)=60.1$  kJ/mol was obtained for the adsorption of AF on the oxidized surface of nickel from the neutral buffer solution. It is higher than  $(-\Delta G_{a, \max}^0)$  on copper (55.4 kJ/mol) and steel St3 (34.95 kJ/mol) under the same conditions.
6. Corrosion tests of Cu in an aqueous 0.01 M NaCl solution showed high protective effects of AF. Complete protection of Cu in this case is observed at 1.5 mmol/L AF (0.88 mg/L). Under more severe conditions (3.5% NaCl), the degree of protection of copper Z is about 60.5%. At 1.0 mmol/L AF on the alloy, Z does not exceed 22% in the entire concentration range studied.

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