Adsorption of 2-mercaptobenzthiazol on copper and MNZh-5-1 alloy and their protection from corrosion in aqueous solutions¹

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Abstract

The adsorption, passivation and protective properties of 3-amino-1,2,4-triazole (3-AT) and 2-mercaptobenzothiazole (2-MBT) on copper and MNZh 5-1 alloy were studied. The adsorption characteristics of both compounds on reduced and oxidized surfaces of copper and its alloy were calculated. On oxide-free surfaces ($E = -0.60$ V) of both metals, physical adsorption of 3-AT and 2-MBT occurs, whereas chemical adsorption occurs on oxidized surfaces ($E = 0.0$ V). The free energies of adsorption calculated by two independent methods, ellipsometry and electrochemical impedance spectroscopy, correlate well with each other. The orientation of the studied compounds on the metal surface was revealed by the ellipsometric method. 2-MBT on reduced and oxidized surfaces of the MNZh 5-1 alloy and copper is adsorbed in planar orientation, forming bonds with the surface through sulfur and nitrogen atoms. 3-AT on cathodically reduced surface of the alloy and copper is in planar orientation, whereas at the anodic potential, in a nearly vertical orientation. 2-MBT is adsorbed on oxidized copper better than 3-AT, apparently due to interaction with its oxide. It allows a protective coating to be formed on the surface that protects the metal well even at high chloride concentrations. Corrosion tests of copper and its alloy in 3.5% sodium chloride solution confirmed the high protective properties of 2-MBT. The created inhibitor mixture of 2-MBT with sodium laurate in equimolar ratio at a total concentration of 0.20 and 0.25 mmol/L allows one to achieve almost complete protection of copper and its alloy with $Z = 99.1$ – 99.3% , respectively.

Keywords: *corrosion inhibitor, degree of protection, ellipsometry, impedance, passivity, free adsorption energy, 3-amino-1,2,4-triazole, 2-mercaptobenzothiazole.*

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Introduction

Due to high electrical and thermal conductivity, copper and its alloys are widely used as structural materials in water cooling systems and in electrical and radio engineering devices, as well as in instrument-making industry [1]. In humid atmospheres, a layer of corrosion products (patina) is formed on copper and partially protects it from corrosion [2]. In an aqueous medium containing corrosive chloride ions, surface activation occurs, which increases the rate of corrosion damage. To protect copper and its alloys, corrosion inhibitors (CIs) are often used under these conditions.

Heterocyclic compounds containing elements such as N, S, and O are often effective CIs due to the interaction of these active centers with copper upon adsorption on the surface of a metal (alloy) and formation of a film of complex compounds with Cu(I). The most widely used CI for copper is 1,2,3-benzotriazole (BTA), which has been known in this function since 1947 [3]. Extensive research and practical application of BTA, as well as other triazoles, have been repeatedly covered in the literature and is currently continuing [4–14]. Recently, however, CIs for copper belonging to the class of triazoles have been criticized because of their high toxicity. In this regard, the authors' claim [15] is noteworthy that in many cases some substituted thiazoles can be excellent replacements for toxic triazoles.

Among the thiazoles used to protect copper, 2-mercaptobenzothiazole (2-MBT) has long been known. Even J. Bregman [16] called 2-MBT the best CI for water recycling systems. It was later confirmed that 2-MBT is one of the best CIs for copper among substituted benzothiazoles in solutions of 0.5 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ with pH 11.4 [17, 18] and much more effective than BTA not only in alkaline but also in acidic environments [19].

In neutral solutions, this CI is studied less thoroughly, apparently due to its low solubility in water that can however be increased by conversion to the sodium salt or by using an additional organic solvent. For example, Japanese researchers [20] showed that 2-MBT forms a protective film on a Cu_2O layer in its solution at $t > 50^\circ\text{C}$. It turned out that it can also be formed at room temperature if acetone (~ 20 wt.%) is added to the solution. The authors noted that 2-MBT is more effective than BTA in the chemical–mechanical polishing of copper, provided that there is no H_2O_2 in the polishing formulation. Kazansky *et. al.* [21], who studied the behavior of copper in a neutral water-ethanol phosphate solution containing 2-MBT, showed that its adsorption occurs with formation of a chemical compound of Cu(I) cations with exo-sulfur and nitrogen atoms of the CI. The protective layer of a copper complex, presumably of polymeric nature $[\text{Cu(I)MBT}]$, reaches a thickness of 8–9 nm after 12 hours of immersion of the electrode to the solution.

The interest in 2-MBT persists in our time. Recently, the *in situ* ellipsometric method, which has proven itself in the study of various organic CIs, was used for the first time to show that 2-MBT adsorption on a pre-oxidized copper electrode at $E = 0.0$ V in a neutral (pH 7.40) borate buffer is described by the logarithmic Temkin equation [22]. The free adsorption energy calculated from it, $(-\Delta G_a^0) > 68$ kJ/mol, is significantly higher than in

the case of BTA and leaves no doubt about the chemisorption of these CIs on the oxidized surface of copper. In [23], 2-MBT was studied as a CI for copper in 3.0% NaCl solution. It was shown that after 100 hours of exposure in the inhibited solution, it reduces the roughness of the metal surface and slows down both electrode reactions, *i.e.* acts as a mixed type CI. The thickness of the protective layer formed by 2-MBT on copper was estimated to be 1.5 ± 0.5 nm.

The results of studying copper alloys in a neutral solution and in the presence of 2-MBT are also noteworthy. In fact, in [24] the surface of brass (80Cu/20Zn) exposed to water and various aqueous solutions was studied by XPS method. Dezincification of the surface layer was observed in pure water and in borate solutions (pH 6.50, 7.40, and 9.10). In contrast, in a 0.5 M solution of NaCl or Na₂SO₄, when brass is exposed to corrosive anions Cl[−] or SO₄^{2−}, copper is removed from the surface layer of brass, *i.e.* its “decopperification” occurs. Exposure of brass in a 0.05 mmol/l 2-MBT solution slows down the oxide growth and results in formation of a complex [Cu_{*x*}Zn_{0.5(1−*x*)}MBT], where $x > 0.5$, possibly of polymer nature, that is capable of protecting copper from corrosion.

The purpose of this article is to study the adsorption of 2-MBT from a borate buffer solution (pH 7.40) on copper, an uncoated oxide film and on MNZh-5-1 alloy, which is often used in heat transfer equipment, as well as the inhibition of corrosion of these structural materials in 3.5% NaCl aqueous a solution with this compound.

Experimental

Studies of the adsorption of commercial compounds, *i.e.*, 3-amino-1,2,4-triazole (3-AT, Sigma Aldrich, CAS 61-82-5, Product of China) and 2-mercaptobenzothiazole (2-MBT, Sigma Aldrich, CAS 149-30-4, Product of China) were carried out by two independent methods in a borate buffer solution with pH 7.40. In one of the methods, the *in situ* ellipsometric method, electrodes made of M-1 copper (Cu+Ag–99.9%, GOST 859-2014) and the MNZh 5-1 alloy (copper-nickel-iron containing more than 90% Cu (GOST 492-2006) were used.

Ellipsometric studies were carried out on an RR 2000 handheld ellipsometer in an electrochemical cell, which makes it possible to simultaneously maintain the electrode potential from the potentiostat PAR model 173 and measure the phase shift angle Δ and polarization restoration angle Ψ .

The accuracy in determining the angles is $\pm 0.05^\circ$. These angles describe the surface of the electrode and depend on its potential and on the solution composition, including the addition of a CI. With a growth of an oxide or adsorption film on the electrode surface, the angle Δ decreases, and the magnitude of the angle change $\delta\Delta$ is proportional to the thickness of the growing film, d . At $d \leq 10$ nm, the Drude equation holds for a uniform film:

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

where α is the proportionality coefficient, Δ_0 is the angle value for the initial surface, and Δ is the angle value during the experiment. To obtain the CI adsorption isotherm, we add its concentrate in portions to the background solution. For each concentration, the Δ angle decreases in time and stops changing after a while. Thus, we determine $(-\delta\Delta)$ to build the dependence of $(-\delta\Delta)$ on the CI concentration, C_{in} . The value of C_{in} at which the changes in the Δ angle cease corresponds to the formation of a monolayer. For this $(-\delta\Delta)$ value, the degree of electrode surface coverage with an adsorbate is $\theta \rightarrow 1$. The experimental dependence of $(-\delta\Delta)$ on $\log C_{in}$ is rearranged into the adsorption isotherm $\theta-f(\log C)$ and the equation describing it is determined. In the cases under consideration, the adsorption of the CI is adequately described by the complete Temkin equation:

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

where f is the surface inhomogeneity 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 associated with the free energy of adsorption by the ratio:

$$B = [\exp(-\Delta G_a^0) / RT] / 55.5 \quad (3).$$

The technique described previously in [11] was used to determine $-\Delta G_{a,\min}^0$, $-\Delta G_{a,\max}^0$, the f coefficient, $B_{\max}$, and $B_{\min}$.

Adsorption studies by the electrochemical impedance spectroscopy (EIS) method were carried out on an M1 copper electrode, which was mounted with epoxy resin into a polypropylene holder so that its working surface was the base of the cylinder ($S_{Cu} = 0.28 \text{ cm}^2$). The electrodes were polished with emery paper of different grades, up to P1000 paper, and then degreased with acetone. All experiments were performed using the Solartron Schlumberger computerized electrochemical interface (United Kingdom), which consists of a 1286 potentiostat and a FRA 1250 frequency response analyzer.

To record the spectrum, we used a glass cell with a volume $V = 0.05 \text{ L}$ with separated cathodic and anodic spaces. Electrochemical impedance spectra were obtained in the frequency range ω from 10 kHz to 0.1 Hz with an voltage amplitude of 10 mV. The working and auxiliary electrodes (a platinum mesh with an area of $S_{Pt} = 20 \text{ cm}^2$) were placed coaxially in the electrochemical cell. The potentials of the copper electrode were measured relative to a silver chloride reference electrode and converted to the normal hydrogen scale. The studies were carried out in borate buffer solution with pH 7.40 under natural aeration.

At the beginning of the measurements, the working electrode was kept in borate buffer solution for 15 min at $E = -0.70 \text{ V}$ in order to remove the air-formed oxide and obtain a clean copper surface. After that it was switched to the working potential and kept for 1 h. Then, the spectrum was recorded in the background solution. After this, when CI

was introduced, the electrode was kept for 1 h in the solution, and a spectrum was obtained at a predetermined C_{in} , which, after reaching a steady-state measured value, was increased by adding a new portion of CI concentrate. To determine the elements of the equivalent electrical circuits (EEC), the results were processed using the *ZView* program.

The degree of coverage of the electrode surface with an inhibitor was calculated by the equation

$$\theta = \frac{C_0 - C_x}{C_0 - C_{max}} \quad (4)$$

where C_0 , C_x , C_{max} – the capacity of the double electric layer (dl), respectively, in the background solution, in the presence of CI in the solution and with the degree of coverage of the surface with the latter close to 1. The value of the capacity of the dl , which no longer decreased with a further increase in the C_{in} in the solution, was taken. The value was calculated in the same way as for the ellipsometry method according to Equations 2, 3 for the Temkin isotherm.

Polarization curves were recorded using an IPC-PRO potentiostat on an electrode made of M1 copper ($S=0.75 \text{ cm}^2$) or MNZh 5-1 alloy ($S=0.50 \text{ cm}^2$) in an electrochemical cell with divided electrode spaces. The working electrode was preliminarily polished on sandpaper with different grain sizes and 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 reported in the standard hydrogen scale. The auxiliary electrode was made of pyrographite.

After removing the air-formed copper oxide film (keeping the electrode for 15 min at $E=-0.65 \text{ V}$ in borate buffer with pH 7.40 containing 0.01 M NaCl), the potentiostat was switched off and a free corrosion potential E_{cor} was established. After the inhibitor was added to the buffer solution and a new E_{cor} value established, polarization curves were recorded at a potential scan rate of 0.2 mV/s. The potential of copper local depassivation by chlorides (E_{ld}) was determined by a sharp increase in current on the polarization curve with subsequent visual identification of pits on the electrode surface. The error in the E_{ld} measurement was 0.01 V. The ability of an inhibitor to prevent local depassivation of copper was determined by the displacement of E_{ld} relative to E_{ld} in the initial borate buffer containing 0.01 mol/l NaCl: $\Delta E = E_{ld}^{in} - E_{ld}^{background}$

Corrosion tests were conducted on plates of M1 copper ($S=38 \text{ cm}^2$) and MNZh-5-1 ($S=25 \text{ cm}^2$) in 3.5% NaCl solution without and with the CI. The corrosion rate was determined gravimetrically, by the decrease in the mass of the sample after 7 days of testing. The degree of protection Z was calculated by the formula

$$Z = \frac{K_0 - K_{in}}{K_0} \cdot 100\% \quad (5)$$

where K_0 is the corrosion rate without the CI and K_{in} is the corrosion rate with the CI.

Results and Discussion

Copper

Adsorption of organic CIs, for example, various azoles [11–13, 18, 22, 25–29], from a borate buffer solution with pH 7.40 on copper was mainly studied *in situ* by ellipsometric method at an electrode potential of $E=0.0$ V. The adsorption studies was often supplemented by results of studying the composition of passivating layers on copper *ex situ* by the XPS method [12, 22, 25, 26, 28, 29]. It was recently shown [28] that additional information on the adsorption of azoles on copper can also be obtained by another *in situ* method – EIS whose measurement results are consistent with ellipsometric adsorption measurements. Based on the calculation results for the EIS and reflection angles for ellipsometry, adsorption isotherms were built for 3-AT and BTA, which showed the similarity of the adsorption measurement results by the two independent methods. In all the cases studied, isotherms were adequately described by Eq. (2). It was shown that at $E=-0.60$ V, 3-AT is adsorbed on the oxide-free surface of copper better than BTA, which, judging by the values of $(-\Delta G_{a, \max}^0)=27$ and 32 kJ/mol calculated from the results of ellipsometric measurements and EIS, respectively, does not give reason to consider its interaction with the surface as chemisorption. The adsorption of 3-AT measured by the EIS method under the same conditions is characterized by $(-\Delta G_{a, \max}^0)=40.8$ kJ/mol, which indicates a high probability of chemisorption of this CI. On a pre-oxidized electrode at $E=0.0$ V, the adsorption of both triazoles also increases, and according to ellipsometric measurements, $(-\Delta G_{a, \max}^0)=52.5$ and 59.3 kJ/mol for BTA and 3-AT, respectively. Thus, despite the greater hydrophilicity of 3-AT compared to BTA, it is more strongly adsorbed on copper, so it is interesting to compare its adsorption with that of 2-MBT.

The Nyquist plots or hodographs obtained by adsorption of 2-MBT on oxidized copper at $E=0.0$ V have the shape of two elongated semicircles (Figure 1a). The first semicircle determines the parameters of the Cu_2O oxide coating formed at this potential, and the second one determines the characteristics of the double layer. These hodographs can be described using the known EEC of an oxide coated electrode [33]. In the EEC of an oxidized copper electrode at $E=0.0$ V in a borate buffer solution with pH 7.4 shown in Figure 1b, R_s , R_c , and R_t are the solution, coating, and charge transfer resistances, and Q_c and Q_{dl} are the coating capacitance and *dl* capacitance, respectively, expressed as constant phase elements. The value of Q_{dl} is related to the true capacity of the double layer by the equation

$$C_{dl} = (Q_{dl} \cdot R_t)^{(1/n)} / R_t$$

where n is a power-law coefficient that takes the surface inhomogeneity into account.

The calculation of the parameters of the adsorption isotherm (Figure 1c, curve 1) shows that the free adsorption energy on the oxidized surface of copper reaches $(-\Delta G_{a, \max}^0)=68.4$ kJ/mol. The results obtained by ellipsometry give values $(-\Delta G_{a, \max}^0)=69.0$ kJ/mol (Table 1), which shows good convergence of the methods of ellipsometry and

EIS in this case. These values of the free energy of adsorption indicate the existence of a chemical interaction of 2-MBT with the oxidized surface of copper at $E=0.0$ V.

Figure 1a. Nyquist plots of oxidized copper electrode at $E=0.0$ V in borate buffer solutions without (1) and with 2-MBT (in mol/l): 2 – $5.0 \cdot 10^{-12}$, 3 – $1.0 \cdot 10^{-11}$, 4 – $1.5 \cdot 10^{-11}$, 5 – $2.0 \cdot 10^{-11}$, 6 – $2.5 \cdot 10^{-11}$, 7 – $3.5 \cdot 10^{-11}$, 8 – $4.9 \cdot 10^{-11}$.

Figure 1b. Equivalent electrical circuit of an oxidized copper electrode at $E = 0.0$ V in a borate buffer solution with pH 7.40.

Figure 1c. The dependence of the degree of surface coverage θ (1) and the resistance of the oxide coating R_c (2) on the logarithm of the concentration of 2-MBT on oxidized copper at $E=0.0$ V in a borate buffer solution, pH 7.40.

Table 1. Adsorption characteristics of 2-MBT and 3-AT on copper and alloy MNZh 5-1 at different potentials in a borate buffer solution with pH 7.40.

Inhibitor	Copper			MNZh 5-1 alloy		
	$(-\Delta G_{a, \min}^0)$ kJ/mol	$(-\Delta G_{a, \max}^0)$ kJ/mol	f	$(-\Delta G_{a, \min}^0)$ kJ/mol	$(-\Delta G_{a, \max}^0)$ kJ/mol	f
$E = -0.60$ V						
2-MBT	36.8	39.2	0.81	41.4	45.6	2.56
3-AT	27.0	28.9	0.72	32.2	34.4	0.91
3-AT (EIS)	33.4	40.8 [28]	2.99	—	—	—
$E = 0.00$ V						
2-MBT	66.7	69.0 [22]	1.46	66.3	71.1	2.68
2-MBT (EIS)	67.2	68.4	0.96			
3-AT	56.0	57.7 [12]	1.02	61.0	68.0	2.80
3- AT (EIS)	54.9	59.3 [28]	1.83			

The calculation of the EEC elements showed that the resistance R_c , which at $E=0.0$ V can be associated with the resistance of Cu_2O , decreases with an increase in C_{in} (Figure 1c, curve 2). This is most likely due to a decrease in oxide thickness. A similar effect of decreasing the intensity of the Auger spectra of Cu_2O , and hence its thickness, upon addition of 2-MBT was observed in [34]. It was shown [35] that the adsorption of sulfur-containing compounds on copper can be associated with the interaction of the thiol group with Cu_2O , as a result of which a copper complex is formed on the surface: $\text{Cu}_2\text{O} + 2\text{RS}^- + \text{H}_2\text{O} \rightarrow 2\text{CuSR} + 2\text{OH}^-$.

Thus, it can be considered as proven that at $E=0.0$ V, 2-MBT is chemisorbed on oxidized copper.

As mentioned above, the adsorption isotherm of 3-AT on copper at $E=-0.60$ V was obtained by the EIS method [28]. In this case, an EEC consisting of one R–CPE chain was used, from which the C_{dl} value was determined. The hodograph obtained upon adsorption of 2-MBT is adequately described only if Warburg impedance is added to the circuit. Because of this, it is not possible to unambiguously calculate the true value of C_{dl} , and, therefore, to build the adsorption isotherm.

Corrosion tests in 3.5% NaCl (Table 2) were carried out in solutions with different pH, since its value varies greatly depending on the concentration of 2-MBT. The values of Z with respect to different backgrounds are given after a slash. One can see that the difference is high at high corrosion rates and almost negligible at low rates. Addition of 2-MBT slow down the corrosion of copper significantly even at $C_{\text{in}}=0.2$ mmol/l, and there is practically no corrosion at 0.4 mmol/l ($Z=98.7\%$).

Table 2. The corrosion rate K and the degree of protection Z for copper samples ($S = 0.0038 \text{ m}^2$) after 7 days of immersion in 3.5% NaCl solution.

Inhibitor	C_{in} , mmol/L	pH solution	K , g/m ² ·days	Degree of protection, Z , %
Without inhibitor/without inhibitor+NaOH	0.00	6.4/9.2	0.75/0.67	–/–
3-AT	0.10	7.25	0.23	69.3/65.7
	0.30	7.31	0.06	92.0/91.0
	0.60	7.35	0.03	96.0/95.9
	1.00	7.38	0.006	99.5/99.1
	1.50	7.40	0.002	99.7/99.7
	2.00	7.42	0.002	99.7/99.7
2-MBT	0.05	7.8	0.55	26.7/18.0
	0.10	8.2	0.42	44.0/37.0
	0.20	8.7	0.04	94.7/94.0
	0.40	9.2	0.01	98.7/98.5
	0.75	9.5	0.01	98.7/98.5
$C_{11}H_{23}COONa$	0.05	9.3	0.20	73.3/70.1
	0.10	9.5	0.17	77.3/74.6
	0.20	9.8	0.16	78.7/76.1
	0.40	9.9	0.13	82.7/80.6
	0.50	10.0	0.12	84.0/82.1
2-MBT+ $C_{11}H_{23}COONa$ (1:1)	0.05	8.7	0.71	5.3/–
	0.10	9.0	0.40	46.7/40.3
	0.15	9.1	0.24	68.0/64.2
	0.20	9.3	0.008	98.9/98.8
	0.30	9.4	0.007	99.1/99.0
	0.40	9.6	0.007	99.1/99.0

It is interesting to compare these results with the protective effect of an organic corrosion inhibitor belonging to another class of compounds, *i.e.*, sodium laurate $C_{11}H_{23}COONa$ (SL). Even at small $C_{\text{in}} = 0.05 \text{ mmol/l}$, it reduces the corrosion rate of copper ~ 4 -fold, but a further increase in C_{in} almost does not change the corrosion rate. In addition, at $C_{\text{SL}} > 0.5 \text{ mmol/l}$ the solubility of the inhibitor decreases due to the “salting-out effect” caused by the high concentration of chlorides. Mixing SL with 2-MBT in an

equimolar ratio makes it possible to achieve $Z=99\%$ at $C_{in}=0.2$ mmol/l, *i.e.* almost complete copper protection. In this case, $C_{2-MBT}=0.1$ mmol/l, *i.e.* it is 4 times smaller compared with a solution in which 2-MBT itself provides the same protective effect.

Table 3. The corrosion rate K and the degree of protection Z for MNZh 5-1 ($S=0.0025$ m²) after 7 days of immersion in 3.5% NaCl solution.

Inhibitor corrosion (CI)	C_{in} , mmol/L	pH solution	Corrosion rate K , g/m ² ·days	Degree of protection Z , %
without CI	0.0	6.4	0.88	–
without CI+NaOH		9.2	0.62	/–
2-MBT	0.25	8.8	0.408	54/34
	0.5	9.3	0.165	81/73.3
	1.0	9.6	0.080	91/87
	1.5	9.7	0.063	93/90
	2.0	9.9	0.028	97/95.5
3-AT	0.5	7.34	0.21	76/66
	1.0	7.38	0.17	81/72.5
	1.5	7.40	0.09	90/82
	2.0	7.42	0.040	95.5/93.5
	3.0	7.43	0.016	98.2/97.4
2-MBT+3-AT (1:1)	0.25	8.62	0.20	77.2
	0.50	8.70	0.06	93/90.3
	1.0	8.82	0.01	98.8/98.4
	2.0	8.98	0.0	100/100
2-MBT+C ₁₁ H ₂₃ COONa (1:1)	0.05	8.7	0.69	6.8
	0.10	9.0	0.39	47
	0.15	9.1	0.19	74
	0.2	9.3	0.048	93.5/92.3
	0.25	9.4	0.005	99.3/99.2
C ₁₁ H ₂₃ COONa	1.0	10.02	1.09	–
	2.0	10.17	0.96	–
	5.0	10.28	0.10	88.6/84
	7.5	10.70	0.06	93.2/90

MNZh 5-1 alloy

The MNZh 5-1 alloy has a higher resistance to the corrosive action of chlorides than copper [22, 30–32]. For example, addition of 20 mmol/l 3-AT is required to suppress the anodic dissolution of copper in a borate buffer containing 10 mmol/l NaCl, which is 2 times higher than the concentration of NaCl. For a similar effect on the alloy, 7 mmol/l 3-AT is sufficient, which is almost 3 times lower than for copper (Figure 2a). Smaller 3-AT concentrations ($C_{in} \geq 0.12$ mmol/l) suppress the first anodic current peak on the polarization curve of the alloy and increase the E_{ld} by at least 0.18 V. Addition of 3.0 and 5.0 mmol/l 3-AT also practically suppresses the second anodic peak and E_{ld} increases by 0.26 and 0.35 V, respectively.

2-MBT begins to exhibit protective properties to copper in a similar solution at $C_{in} = 1.1$ mmol/l [22]. On the MNZh 5-1 alloy, 0.10 mmol/l is sufficient to suppress the first anodic peak, and a further increase in C_{in} shifts E_{ld} in the positive direction and reduces the current densities of both peaks until they disappear at $C_{in} = 0.15$ mmol/l (Figure 2b). At 0.25 mmol/l, 2-MBT forms such a stable passive film that it prevents not only local depassivation but also anodic oxygen evolution.

The use of equimolar formulations of 2-MBT with sodium laurate (Figure 2c) and 3-AT (Figure 2d) leads to the protection of the MNZh 5-1 alloy from local depassivation in chloride buffer solution at lower concentrations than 3-AT and sodium laurate individually.

The ability of the studied compounds to passivate the alloy at such low C_{in} is undoubtedly associated with their strong adsorption on the surface to be protected and the formation of hardly soluble complex compounds with the metals that constitute the alloy, primarily with Cu(I). It is possible to estimate the free adsorption energy during the formation of the first monolayer on the alloy surface using the *in situ* ellipsometric method. At the same time, it is possible to compare their adsorption at different electrode potentials, which allows us to evaluate the effect of the state of the alloy surface on adsorption: at $E = -0.60$ V, when it is free of oxides, and at $E = 0.0$ V on a pre-oxidized alloy surface.

On the oxide-free copper surface, the adsorption of both compounds under study begins at C_{in} : 0.08 mmol/l for 3-AT and 0.004 mmol/l for 2-MBT (Figures 3 and 4). The adsorption of these compounds on the alloy begins at lower C_{in} : this is $C_{in} = 0.056$ mmol/l for 3-AT and $C_{in} = 0.4$ mmol/l for 2-MBT.

This was to be expected from a comparison of the anodic polarization curves of the alloy and copper [22]. For 3-AT adsorption on the alloy at $E = -0.60$ V, the first small plateau of $(-\delta\Delta)$ at $0.17\text{--}0.18^\circ$ can be distinguished, which is shown in Figure 3a with a dashed line. It may correspond to a monolayer surface coverage. The values of $(-\Delta G_{a, \max}^0)$ calculated by Equation 2 for 2-MBT and 3-AT are given in Table 1. The free adsorption energy of 2-MBT is 39.2 kJ/mol, which is by 10 kJ/mol higher than that of 3-AT.

Figure 2. Polarization curves of MNZH 5-1 in a borate buffer with pH 7.40, containing: (1) 10 mmol/l of NaCl with and without added inhibitor, C_{in} (in mmol/l): 3-AT: 2 – 0.12; 3 – 0.25; 4 – 0.50; 5 – 1.5; 6 – 3.0; 7 – 5.0; 8 – 7.0; 2-MBT: 2 – 0.03; 3 – 0.06; 4 – 0.10; 5 – 0.15; 6 – 0.25; 2-MBT + $C_{11}H_{23}COONa$ (1:1): 2 – 0.06; 3 – 0.08; 4 – 0.20; 5 – 0.25; 2-MBT + 3-AT (1:1): 2 – 0.13; 3 – 0.25; 4 – 0.50.

Figure 3. Dependence of the change in the ellipsometric angle (Δ) (a) and the degree of surface coverage θ (b) on the logarithm of 3-AT concentration on reduced surface of MNZh 5-1 alloy (1) and copper (2) [12] at $E = -0.60$ V in borate buffer solution with pH 7.40.

Figure 4. Dependence of the change in the ellipsometric angle (Δ) (a) and the degree of surface coverage θ (b) on the logarithm of 2-MBT concentration on reduced surfaces of the MNZh 5-1 alloy (1) and copper (2) at $E = -0.60$ V in borate buffer with pH 7.40.

It is interesting that the factor of surface heterogeneity f sharply increases in the case of adsorption of 2-MBT on the alloy compared with adsorption on copper. The adsorption of 3-AT is less sensitive to changes on the reduced electrode surface on passage from copper to the alloy.

If cuprite Cu_2O is already present on the surface of copper and alloy at $E = 0.0$ V, then this can improve the adsorption of 3-AT and 2-MBT (Figure 5). The isotherms of these compounds originate in the region of lower C_{in} than for the oxide-free surface. For 3-AT on the surface of MNZh 5-1 and copper at $E = 0.0$ V, adsorption begins at C_{in} values that are by several orders of magnitude smaller and is characterized by $(-\Delta G_{\text{a, max}}^0) = 68$ and 59 kJ/mol, respectively (Table 1). This is 2 times higher for both metals than for 3-AT adsorption on the reduced surface.

Adsorption on oxidized copper is also characterized by a larger $(-\Delta G_{\text{a, max}}^0)$ value than on reduced surface, also 2.2 times for 3-AT and 1.95 times for 2-MBT. The f coefficient in these cases also becomes higher, which is especially pronounced in the case of 3-AT, which, apparently, acquires the ability to be strongly chemisorbed on oxidized surfaces.

The thicknesses of 3-AT and 2-MBT monolayers on the surface of copper and MNZh 5-1 alloy were determined from the results of ellipsometric measurements according to the technique described previously [11]. The proportionality coefficient in Equation (1) is $\alpha = 0.89$ nm/deg for copper and $\alpha = 0.77$ nm/deg for the alloy. The thicknesses obtained on the oxidized surface of the MNZh 5-1 alloy were as follows: $(-\delta\Delta = 0.44^\circ)$, $d = 0.34 \pm 0.1$ nm for 3-AT and $(-\delta\Delta = 0.49^\circ)$, $d = 0.37 \pm 0.1$ nm for 2-MBT. The sizes of the molecules of these inhibitors calculated from the bond lengths of their constituents are 0.50–0.60 nm for 3-AT and 0.82 nm for 2-MBT [22]. It can be assumed that the 3-AT molecule is in an upright position in the monolayer, and 2-MBT is adsorbed in a more planar manner by forming bonds with the copper surface through a nitrogen atom and an

exo-sulfur atom. This regularity also repeats on the oxidized surface of copper: 3-AT is vertically located in a monolayer [12] whereas 2-MBT is in a more slanted position [22].

Figure 5. Dependence of the change in the ellipsometric angle (Δ) (a) and the degree of surface coverage θ (b) on the logarithm of 2-MBT (1) and 3-AT concentrations (2) on the oxidized surface of the MNZh 5-1 alloy at $E = 0.0$ V in borate buffer, pH 7.40.

On oxide-free surfaces of copper and alloy, the thickness of the monolayers is smaller. The thickness of the conditional 3-AT monolayer is ($-\delta\Delta = 0.18^\circ$), $d = 0.14 \pm 0.1$ nm on MNZh 5-1 and ($-\delta\Delta = 0.20^\circ$), $d = 0.20 \pm 0.1$ nm on copper. These values indicate an almost planar arrangement of 3-AT on a “clean” surface. For 2-MBT, the thickness of the conditional monolayer little differs on the alloy and copper ($-\delta\Delta = 0.44^\circ$), $d = 0.34\text{--}0.4 \pm 0.1$ nm and corresponds to a more horizontal arrangement of molecules in the monolayer.

Gravimetric corrosion tests on MNZh 5-1 plates showed that at $C_{\text{in}} = 0.50$ mmol/l, the corrosion rate is reduced 5-fold by 2-MBT and 4-fold by 3-AT. At almost all of the C_{in} values studied, 2-MBT shows the best protection, while the corrosion rate K and degree of protection Z have a more significant tendency to decrease than at similar 3-AT concentrations. At $C_{\text{in}} = 2$ mmol/l, the degree of protection reaches 97% and 95.5% for 2-MBT and 3-AT, respectively.

An equimolar mixture of 2-MBT+3-AT reduces the corrosion rate 4-fold at $C_{\text{in}} = 0.25$ mmol/l and 16-fold at 0.50 mmol/l compared with the uninhibited solution. It should be noted that the mixture is more efficient than each of the components alone. For example, at $C_{\text{in}} = 1.0$ mmol/l, the degree of protection provided by 2-MBT is $Z = 91\%$, that of 3-AT is $Z = 81\%$, while their formulation provides 98.8%.

Another equimolar formulation of 2-MBT with sodium laurate also shows a high degree of corrosion protection in 3.5% sodium chloride solution. 0.25 mmol/l of this mixture is sufficient to obtain almost complete protection of MNZh 5-1, namely, $Z = 99.3\%$. The 2-MBT+ $\text{C}_{11}\text{H}_{23}\text{COONa}$ mixture (1:1) significantly exceeds its components.

Both developed formulations efficiently protect the alloy from corrosion damage in corrosive sodium chloride solution. The formulation of 2-MBT with sodium laurate is more efficient than 2-MBT + 3-AT.

Conclusions

1. A combination of electrochemical, ellipsometric and gravimetric studies showed that 2-MBT is a more efficient corrosion inhibitor of copper and MNZh 5-1 alloy than 3-AT in a neutral chloride solution.
2. 2-MBT is adsorbed on oxidized copper better than 3-AT, apparently due to interaction with its oxide, which allows it to form the protective coating on the surface that protects the metal well even at high chloride concentrations.
3. The studied inhibitors form a monolayer on reduced copper surface, while on the alloy, complex compounds continue to grow after the formation of a conditional monolayer. The 2-MBT molecule is adsorbed in planar orientation on reduced and oxidized surfaces of copper and MNZh 5-1, forming bonds with the surface through sulfur and nitrogen atoms. The 3-AT molecule on the oxide-free surfaces of the alloy and copper is in a planar orientation, but at the anodic potential it is in a nearly vertical position.
4. An equimolar formulation of 2-MBT+sodium laurate was developed, which showed high efficiency for copper and its alloy in 3.5% sodium chloride solution.

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