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Protection of CuSn6 bronze from atmospheric corrosion by an imidazole based corrosion inhibitor

The CuSn6 bronze is a copper alloy with good corrosion resistance and strength properties. It is wear-resistant and well solderable and it is good for cold forming. Springs of all kinds, especially for the electrical industry, are made of this bronze. It is used in paper, pulp and chemical industries, shipbuilding and mechanical engineering.

When exposed to urban atmospheres copper and its alloys are endangered from corroding with time. Thus additional protection is needed. One possibility of protection is the use of corrosion inhibitors. Previous investigations have shown that imidazole derivatives offer good protection in different media.

Potentiodynamic measurements and electrochemical impedance spectroscopy (EIS) were applied to evaluate the inhibitive efficiency of 1-H benzimidazole (BZI) as a corrosion inhibitor for CuSn6 bronze in a $Na_2SO_4/NaHCO_3$ solution which simulates an urban atmosphere. The investigations have shown that BZI is a mixed corrosion inhibitor with good protective properties. The interaction between the inhibitors and the bronze surface is a combination of physisoption and chemical adsorption.

However, after long immersion (over 1 month) the surface colour of bronze changes into a brown-reddish colour. Therefore, this inhibitor cannot be applied at present time to protect objects of which the appereance should not be changed.

1. INTRODUCTION

Copper is technically probably the most important metal after iron. The earth's crest has only 10^{-4} wt-% copper. Though the content of copper is small, copper-bearing mines are well located, so it is relatively easy to extract them [1]. The world copper production was almost 18.5 million tons in 2008 [2].

Copper is found in nature with elements such as lead, nickel, silver, and zinc. It is widely used in industry both as a pure metal and as an alloying element. It is a metal with characteristic light reddish colour, ductile and well recyclable. This metal exhibits excellent electrical and heat conductivities, high resistance towards corrosion and good mechanical properties. Copper has, after silver, the best electrical conductivity. This is the reason why electrical and electronic industries are probably the main field of its application [1, 3].

Roughly speaking, bronzes are copper alloys in which the major alloying element is not zinc or nickel. Nowadays, the term bronze is used with other alloying elements. Bronzes are unquestionably one of the most versatile classes of corrosion- and wear-resistant materials, offering a broad range of properties from a wide selection of alloys and compositions. Tin bronzes can contain between 1 and 10% tin.

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The CuSn6 bronze has 6%-wt content of tin and has good corrosion resistance and strength properties. It is wear-resistant and well solderable and it is good for cold forming. Springs of all kinds, especially for the electrical industry, are made of the CuSn6 bronze. It is used in paper, pulp and chemical industries, shipbuilding and mechanical engineering.

In open air, on their surface a green film of corrosion products called patina is formed. This film in its most stable form, consists of basic copper sulfate, $CuSO_4.3Cu(OH)_2$, although in industrial areas it may contain carbonate, or chloride in marine environments. A small amount of copper dissolves in water that runs over the metal surface, and this can precipitate on to other less noble metals downstream in the water cycle, leading to galvanic corrosion [4,5].

When exposed to urban atmospheres copper and its alloys are endangered from dissolving with time. This is the reason why additional protection is needed. One possibility of protection is the use of corrosion inhibitors.

Azole-type organic compounds have good characteristics as corrosion inhibitors for copper and copper alloys, but since they are often toxic new corrosion inhibitors are being developed. Our previous investigations [6-12] on the efficiency of imidazole derivatives as copper corrosion inhibitors have shown that these compounds offer good protection in different media such as inorganic acid, neutral media (NaCl) and atmospheric corrosion.

2. EXPERIMENTAL

The investigations were performed on the CuSn6 (wt%) bronze. The composition of this alloy, determined according to DIN 17660 is given in Table 1.

Table 1: Elemental composition of the CuSn6 bronze

	Sn	Pb	Zn	Fe	P	Cu
wt-%	6.10	0.01	0.10	0.02	0.11	93.66
at-%	3.36	0.01	0.10	0.02	0.23	96.28

The tested corrosion inhibitor was 1-*H* benzimidazole (BZI), whose molecular structure is shown in Fig. 1. This compound was dissolved in the test solution at different concentrations.

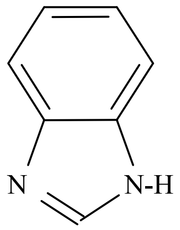

Figure 1: 1-H Benzimidazole (BZI) used as the corrosion inhibitor.

Corrosion resistance of the CuSn6 bronze unprotected and protected by the investigated inhibitor was performed by potentiodynamic polarization in wide (±150 mV vs. E_{corr}) and narrow (±20 mV vs. E_{corr}) potential range and electrochemical impedance spectroscopy (EIS) (at E_{corr} in the frequency range 100 kHz-0.01Hz). They were conducted using a PAR 263A potentiostat/galvanostat and frequency response detector PAR 1025. Measurements were conducted after 1 hour immersion in stirred 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$ solution acidified to pH 5 by addition of dilute sulphuric acid at room temperature. This solution simulates the atmosphere in an urban environment.

3. RESULTS

Results obtained by the anodic and cathodic polarization of the bronze electrode in wide potential range (Fig. 2) show that with addition of inhibitor both anodic and cathodic curves move towards smaller current densities indicating a mixed inhibitor property of BZI. It can be remarked also that the inhibitive effect on the cathodic process seems to no longer improve above 0.5 mmol·dm^{-3}. As for the anodic process, the current density continues, though moderately, to decrease. As a whole, the addition of inhibitor does not modify significantly the corrosion potential. Corrosion parameters evaluated from these curves are presented in Table 2.

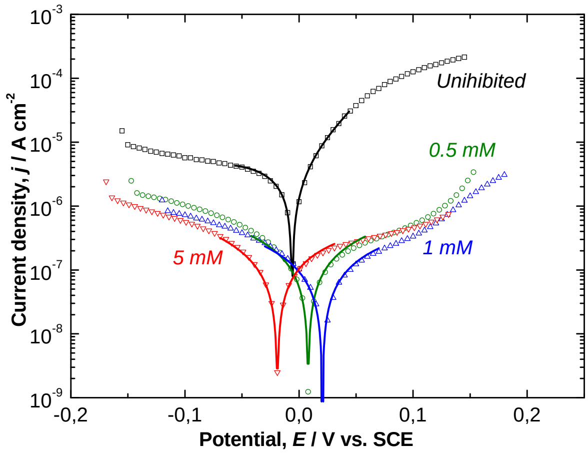

Figure 2: Wide range polarization curves of bronze electrode in Na_2SO_4 / $NaHCO_3$ with different BZI concentrations.

The corrosion current density presented in Table 2 decreases markedly in presence of the corrosion inhibitor even at very low concentrations, and is the smallest at the concentrations between 0.05 to 1 mmol·dm^{-3}. Further addition of inhibitor does not deteriorate the inhibitive efficiency. The inhibitive efficiency reaches 93 %.

Table 2: Corrosion parameters of bronze in Na_2SO_4 / $NaHCO_3$ with different BZI concentrations, determined by the Tafel extrapolation method.

c, mmol·dm^{-3}	/	0.001	0.005	0.01	0.05	0.1	0.5	1	5
E_{corr}, mV	-6.40	-31.0	-28.9	-6.03	26.7	-13.0	8.14	20.8	-18.3
b_a, mV·dec^{-1}	54.1	40.4	36.2	38.2	53.7	66.6	121	111	339
- b_c, mV·dec^{-1}	736	362	350	163	177	172	98.4	263	282
j_{corr}, μA·cm^{-2}	4.01	2.39	1.60	0.590	0.301	0.330	0.511	0.402	0.451
z, %	/	40.4	60.1	85.3	92.5	91.8	87.3	90.0	88.8

Corrosion parameters of the bronze electrode obtained from the polarization of bronze in a narrow potential range are displayed in Table 3.

Table 3: Corrosion parameters of bronze in Na_2SO_4 / $NaHCO_3$ with different BZI concentrations, determined by the polarization resistance method.

c, mmol·dm^{-3}	/	**0.001**	**0.005**	**0.01**	**0.05**	**0.1**	**0.5**	**1**	**5**
E_{corr}, mV	-7.00	-28.1	-27.3	-18.1	12.9	-10.1	2.99	1.10	-21.3
B, mV	21.9	15.6	14.3	12.6	17.2	20.3	25.7	16.5	48.5
R_p, kΩ·cm^2	4.50	5.21	6.20	21.0	28.6	67.5	197.2	165.0	243
j_{corr}, A·cm^{-2}	4.87	3.00	2.28	0.600	0.600	0.321	0.135	0.331	0.321
z, %	/	38.4	52.8	87.7	87.7	93.4	97.2	93.2	93.4

It can be seen that the value of polarization resistance increases in presence of inhibitor above 0.01 mmol·dm^{-3}, at which the inhibitive efficiency reaches ca. 87 %. It is important to emphasize that BZI decreases the corrosion current density at the concentration as low as 1 µmol·dm^{-3}. The concentration 0.1 mmol·dm^{-3} is sufficient to obtain marked inhibitive effect.

From the data obtained by the Tafel extrapolation method, the fractional surface coverage, θ, was calculated for each inhibitor concentration, c, and fitted with various isotherms with respect to BZI concentration domain where the inhibitive effect improved with increasing inhibitor concentration, i.e. up to the optimal concentration, $c \leq 0.5$ mmol dm^{-3}. The best fit was obtained with the Langmuir isotherm, as is shown in Fig. 3 [13].

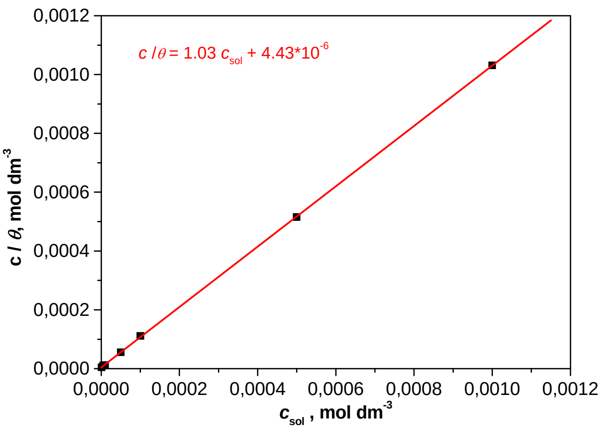

Figure 3: Langmuir adsorption isotherm for bronze in Na_2SO_4 / $NaHCO_3$ in presence of BZI.

The adsorption energy determined from the Langmuir isotherm values [13, 14]:

$$\Delta G_{ads} = -40.5\ kJ{\cdot}mol^{-1}$$

It is negative which reveals the spontaneity of the adsorption process and the stability of the adsorbed layer on the bronze surface. This value is usually accepted as a threshold value between chemisorption and physisorption. This means that BZI connects to the surface partially by electrostatic interaction between the charged molecules and the charged metal (Van der Waals force), physisorption, and partially by charge sharing or transfer from organic molecules to the metal surface forming a coordinate type of bond, chemisorption [15].

Fig. 4 shows the results obtained by the electrochemical impedance spectroscopy.

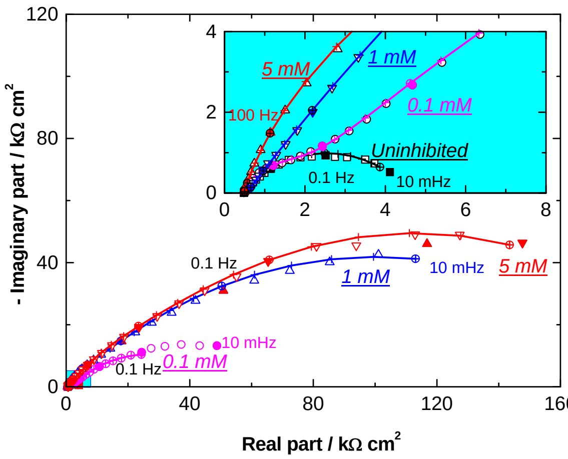

Figure 4: Impedance spectra for bronze in Na_2SO_4 / $NaHCO_3$ with different BZI concentrations.

The impedance spectra are very depressed even in presence of inhibitor. However, two capacitive loops with small Cole-Cole coefficients are sufficient to reproduce suitably the experimental spectrum according to the regression calculation with a Simplex method. The electrochemical process involves therefore only one reaction intermediate in addition to the contribution of the double layer capacitance [16-18]. For the regression calculation of this data the Cole-Cole type distribution was used as illustrated in Fig. 5. For the sake of simplicity, this circuit will be named 2RC.

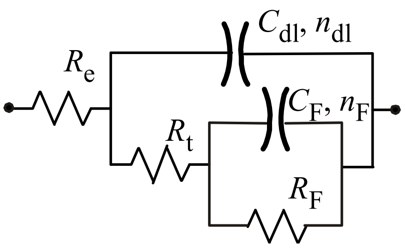

Figure 5: Equivalent electrical circuit (2RC) to represent experimental data. —)(— indicates frequency distributed system coupled with its parallel resistance.

Lines with cross in Fig. 5 are the calculated data. It can be seen that the used model reproduces suitably the experimental data attesting the validity of the adopted equivalent circuit.

The results of regression calculations are summarized in Fig. 6. By using the Stern-Geary relationship with polarization resistance $R_p = (R_t + R_F)$ the corrosion current density was calculated, then the inhibitive efficiency of BZI in the sulphate – carbonate solution was evaluated. The value of the double layer capacitance, C_{dl}, is around a few μF·cm^{-2}, markedly smaller than that expected for this dilute solution medium. The surface coverage by BZI may modify deeply the double layer structure. This high adsorption effect is really reflected by good inhibiting efficiency, z, observed for the coupling Na_2SO_4 / $NaHCO_3$ solution – BZI even at very low inhibitor concentrations. C_F is also small, a few tens μF·cm^{-2}, that indicates an efficient inhibitive effect towards the redox process taking place at the electrode surface. Very small values observed at the concentration of 0.1 mmol·dm^{-3} will be considered to be due to a poor separation of two capacitive loops.

The resistances, especially the polarization resistance, are high, greater than 100 kΩ·cm^2. This very high R_p value is in agreement with that determined by the linear polarization method presented above. n_d and n_F are both small, especially when inhibitor concentration is high, that is, in spite of a good inhibiting effect, the surface reactivity is highly distributed. The protective effect is high, and above 90 % for concentrations higher than 1 mmol·dm^{-3} and j_c remains small in the whole concentration domain examined.

Benzimidazole exhibits very good protection properties, as well for the inhibitive efficiency as it maintained for an excess addition to the corrosive medium. According to Material Safety Data Sheet, BZI is just harmful. However, it should be mentioned that after long immersion (over 1 month), its surface colour changes into a brown-reddish colour. Therefore, this inhibitor cannot be applied at present time to protect metal objects of which the appearance should not be changed.

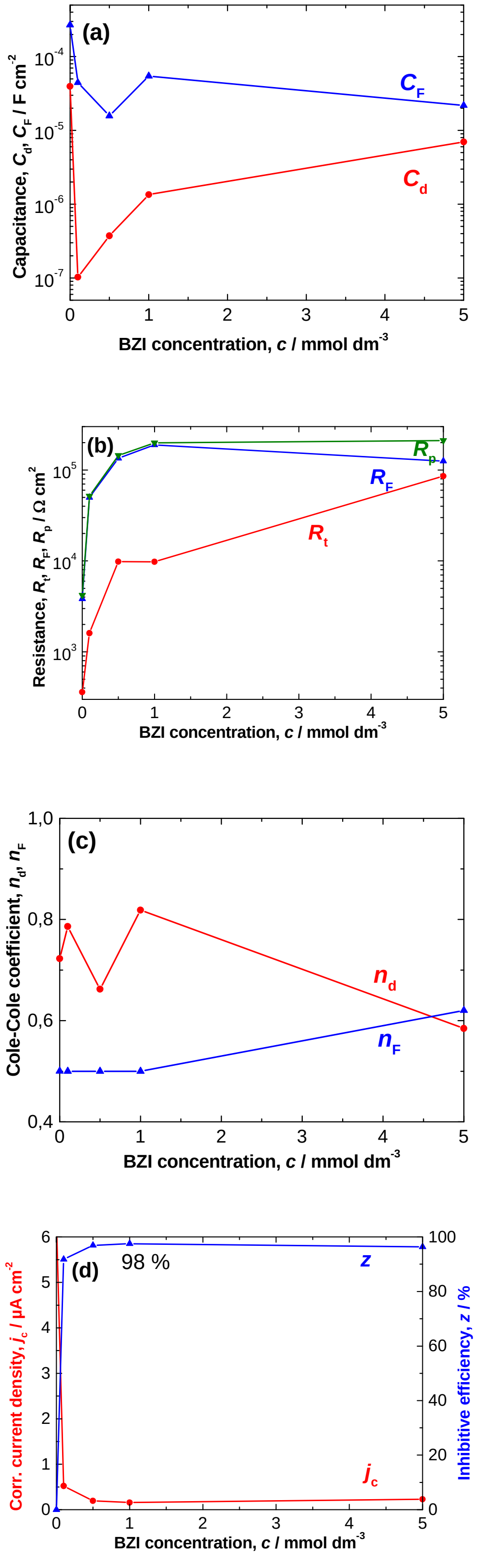

Figure 6: EIS data for bronze in Na_2SO_4 / $NaHCO_3$ with different BZI concentrations.

4. CONCLUSIONS

Different electrochemical methods were applied to evaluate the inhibitive efficiency of 1-*H* benzimidazole (BZI) as a corrosion inhibitor for CuSn6 bronze in 0.2 g·dm^{-3} Na_2SO_4 + 0.2 g·dm^{-3} $NaHCO_3$ at pH 5, which simulates an urban atmosphere.

The investigations have shown that BZI is a mixed corrosion inhibitor. In the investigated solution the concentration of only 0.1 mmol·dm^{-3} is sufficient to obtain a marked inhibiting effect (above 90%). The interaction between the inhibitors and the bronze surface is a combination of physisoption and chemical adsorption.

The impedance spectroscopy measurements have shown that the surface coverage by BZI may modify deeply the double layer structure. This high adsorption effect is really reflected by good inhibiting efficiency, *z*, observed for the coupling Na_2SO_4 / $NaHCO_3$ solution – BZI even at very low inhibitor concentrations. An efficient inhibitive effect towards the redox process taking place at the electrode surface was also observed.

However, after long immersion (over 1 month) the surface colour of bronze changes into a brown-reddish colour. Therefore, this inhibitor cannot be applied at present time to protect objects of which the appereance should not be changed.

Three corrosion evaluation methods (Tafel extrapolation, linear polarization, and electrochemical impedance spectroscopy) exhibited coherent results.

5. LITERATURE

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