Bronze Protection in Seawater

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The aim of this work was to investigate corrosion and protection of bronze in artificial seawater. Corrosion in seawater is a big problem. The presence of high concentration of chlorides results in an extremely high level of corrosion.
Possibility of bronze protection was examined by the use of three different corrosion inhibitors. One of them is traditional benzotriazole (BTA) which is very good corrosion inhibitor but it is toxic. In this study benzotriazole was used in order to compare with the efficiency of two new non-toxic corrosion inhibitors: 1-phenyl-4-methyl-imidazole (PI) and vapor phase corrosion inhibitor (VpCI) which is developed from the fermentation process of sugar beats. Investigation was performed by the means of electrochemical methods (AC and DC techniques).
Tested corrosion inhibitors show high inhibiting efficiency, which in some cases reaches 99%. These results confirmed that in highly aggressive media like seawater benzotriazole can be replaced with environmental friendly corrosion inhibitors which provide the same or even better corrosion protection of bronze.

1. Introduction

Corrosion is unintentional destruction of structural materials caused by physical, chemical and biological agents (1), consisted of a set of chemical and electrochemical processes during which the metal passes from the elemental state to the compounds which are commonly found in nature. It means that corrosion is a spontaneous process which can not be prevented, but it can be slowed down.

Corrosion is one of the important factors of growth rates of materials and energy consumption at the global level and has caused substantial material losses in the economy. One of the research shows that direct costs of corrosion in the United States (substitute of corroded equipment, maintenance and protection of materials), amounts to 3.1% of GDP or U.S. $ 276 billion per year (2). These costs are even greater, because they do not include secondary damage from corrosion, such as stopping production facility, product loss (leakage from tanks and pipelines), reducing the degree of usability - efficiency, pollution or contamination of products, environmental pollution, endangered people's lives, deterioration of cultural heritage, etc.

Bronze is copper alloy (min. 60%) and other elements such as tin, aluminum, silicon, lead, phosphorus, etc. which are added to enhance the mechanical characteristics of alloys. Bronze is much more stable than the copper in highly aggressive media like seawater. The use of bronze is based on good electrical and thermal conductivity, resistance to corrosion and good mechanical properties.

The aim of this work was to examine the corrosion of bronze due to destructive activity of chloride ions in seawater and the possibility of bronze protection with environmental friendly inhibitors.

Corrosion inhibitor is a chemical substance which, when added in small concentration to environment, minimizes or prevents corrosion (3). Disadvantage of some highly effective inhibitors is their toxicity. The wide application in industrial processes requires replacement of toxic inhibitors with nontoxic ones. Therefore numerous studies are being conducted whose aim is to find new non-toxic inhibitors that can protect metal with the same high effectiveness.

Three different inhibitors were examined in this research. One of them is benzotriazole (BTA) which is one of the most important inhibitors for copper and copper alloys (4-6). However, a major deficiency of BTA is its toxicity. Benzotriazole was used in order to compare with the efficiency of two new non-toxic corrosion inhibitors: 1-phenyl-4-methyl-imidazole (PI) and vapor phase corrosion inhibitor (VpCI) which is developed from the fermentation process of sugar beats.

Previous investigations have shown that imidazole derivates have good inhibiting properties with respect to the atmospheric (7), acidic (8-9) and near neutral media (10) copper corrosion, and that they are also environmental friendly (8).

2. Experimental

2.1. Materials

In this research artificial seawater (composition shown in Figure 1) was used as electrolyte.

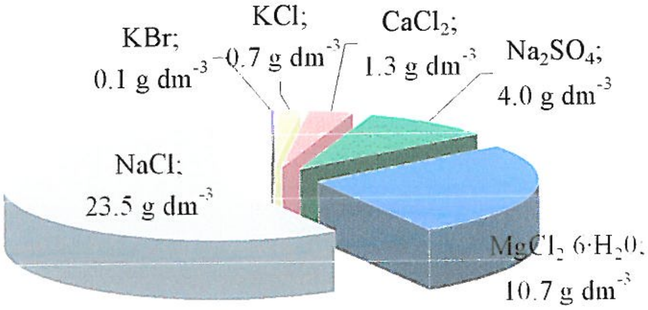

Figure 1. Artificial seawater composition

Examined inhibitors were: 1. vapor phase corrosion inhibitor (*VpCI*), based on the sugar beets, 2.1-phenyl-4-methyl-imidazole (*PI*) and 3.benzotriazole (*BTA*)

Measurements were performed on the bronze samples whose composition is shown in Table I.

TABLE I. Composition of the bronze

wt%	**% Cu**	**% Sn**	**% Zn**
CuSn6Zn	88	6	6

Electrochemical measurements were performed in a three electrodes cell, filled with 300 mL of electrolyte solution. As working electrode was used bronze CuSn6Zn electrode, reference electrode was saturated calomel electrode and counter electrode was highly saturated graphite electrode.

2.2. Methods

Electrochemical methods used in this work were Tafel extrapolation method, linear polarization method and electrochemical impedance spectroscopy.

Polarization resistance determination
The polarization curves were obtained by scanning the potential at the scan rate of 0.166 mV s^{-1} going from initial potential of -20 mV vs. OC (open circuit potential) to +20 mV vs. OC.

Tafel extrapolation method
The polarization curves were obtained by scanning the potential at the scan rate of 0.166 mV s^{-1} going from initial potential of -250 mV vs. OC (open circuit potential) to +250 mV vs. OC. Polarization measurements were performed on VersaStat, EG&G Instrument controlled with model 352/252 SoftCorr ™ Corrosion software.

Electrochemical impedance spectroscopy (EIS)
EIS measurements were performed at the corrosion potential in the frequency range of 10^5 Hz to 10^{-2} Hz with seven points per decade under excitation of sinusoidal wave of 7mV amplitude. Measurements were performed on Gamry PCI4 Potentiostat/ Galvanostat/ZRA with EIS300 software.

3. Results and Discussion

3.1. Tafel extrapolation method

Polarization measurements were performed in wider potential range in order to observe more clearly the influence of corrosion inhibitors on anodic and cathodic polarization curves.

VpCI

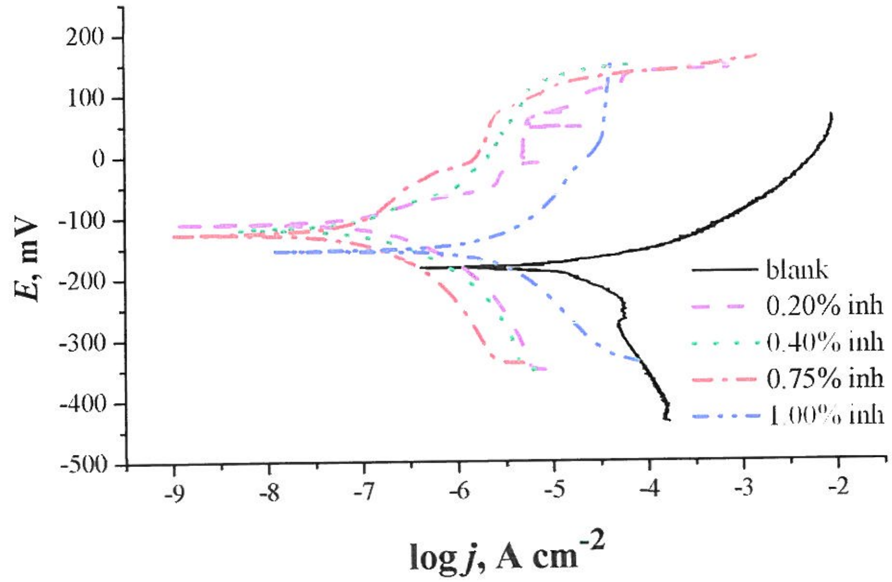

Figure 2. Anodic and cathodic Tafel curves for bronze in artifical seawater without and with the addition of different concentrations of inhibitor VpCI.

Polarization curves obtained for bronze in artificial seawater and in the presence of different concentrations of inhibitor VpCI are shown in Figure 2. Corrosion parameters determined by the Tafel extrapolation method are shown in Table II. The optimum concentration for *VpCI* is 0.75 vol. % (inhibiting efficiency: 99.7%). It is interesting to note that an increase in inhibitor concentration causes shift of corrosion potential towards more positive values which shows that inhibitor VpCI has stronger influence on anodic corrosion process than on the cathodic corrosion process.

TABLE II. Corrosion parameters for bronze in artificial seawater without and with the addition of different concentrations of inhibitor VpCI, obtained by Tafel extrapolation method

c_{inh}, vol %	j_{corr}, μA cm^{-2}	*corr. rate*, μm year^{-1}	E_{corr}, mV	b_a, mV dec^{-1}	b_c, mV dec^{-1}	Z_{inh}, %
-	32.02	756	-191	62	-224	-
0.20	4.69	111	-155	212	-197	85.3
0.40	0.33	8	-119	170	-150	98.9
0.75	0.09	2	-126	117	-86	99.7
1.00	5.95	141	-155	249	-251	81.4

1-phenyl-4-methyl-imidazole (PI)

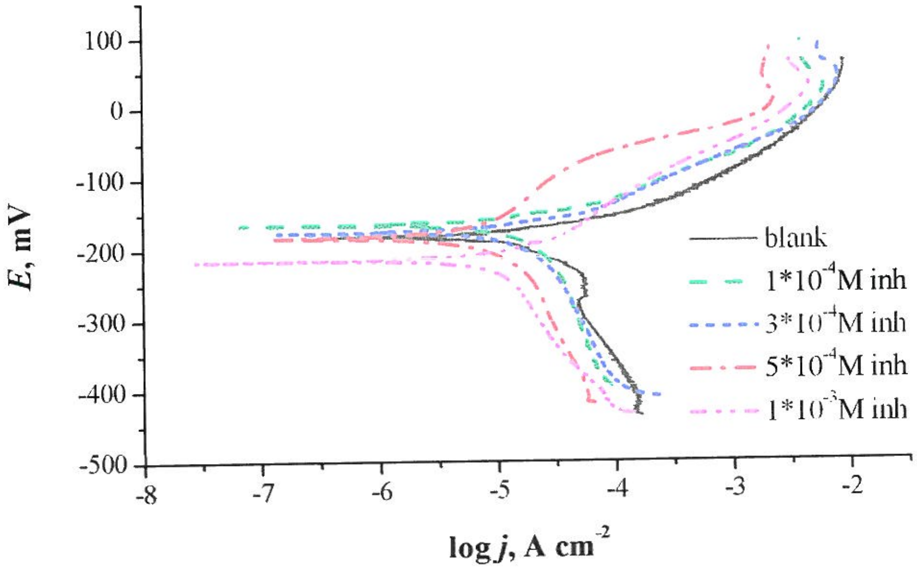

Figure 3. Anodic and cathodic Tafel curves for bronze in artificial seawater without and with the addition of different concentrations of inhibitor 1-phenyl-4 methyl imidazole

Polarization curves obtained for bronze in artificial seawater and in the presence of different concentrations of inhibitor PI are shown in Figure 3. Polarization curve shifted to the left with addition of inhibitor, which means that the inhibitor is effective because it reduces the rate of corrosion of bronze. The presence of inhibitor leads to reduction of anodic and cathode currents, indicating that the PI is mixed type inhibitor.

TABLE III. Corrosion parameters for bronze in artificial seawater without and with addition of different concentrations of inhibitor 1-phenyl-4-methyl-imidazole (PI), obtained by Tafel extrapolation method

c_{inh}, mol dm^{-3}	j_{corr}, µA cm^{-2}	*corr. rate*, µm year^{-1}	E_{corr}, mV	b_a, mV dec^{-1}	b_c, mV dec^{-1}	Z_{inh}, %
-	32.02	756	-191	62	-224	-
$1\cdot10^{-4}$	17.13	404	-166	45	-275	46.5
$3\cdot10^{-4}$	14.70	347	-178	44	-181	54.1
$5\cdot10^{-4}$	5.45	128	-184	89	-164	83.0
$1\cdot10^{-3}$	14.47	342	-217	107	-294	54.8

From the values of corrosion current density it can be concluded that corrosion rate decreases in the presence of PI. In the studied concentration interval, the lowest rate of corrosion is 128 μm year^{-1} observed at inhibitor concentration of $5 \cdot 10^{-4}$ mol dm^{-3}. The effectiveness of inhibitors in this case is 83%.

benzotriazole (BTA)

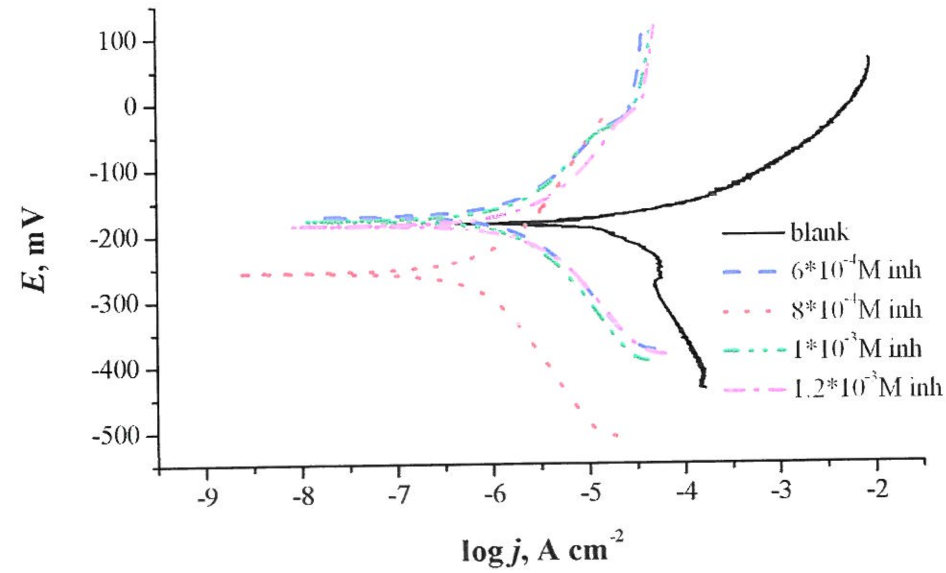

Figure 4. Anodic and cathodic Tafel curves for bronze in artificial seawater without and with the addition of different concentrations of inhibitor benzotriazole (BTA)

The maximum efficiency of BTA was obtained at relatively low inhibitor concentration $8 \cdot 10^{-4}$ mol dm^{-3} but it was higher than the optimal concentration of PI. Studies performed in the presence of BTA (Figure 4. and Table IV.) show that this compound behaves similarly to inhibitor VpCI and inhibitor PI. The highest efficiency obtained was 97.3%

TABLE IV. Corrosion parameters for bronze in artificial seawater without and with the addition of different concentrations of inhibitor benzotriazole (BTA), obtained by Tafel extrapolation method

c_{inh}, mol dm^{-3}	j_{corr}, μA cm^{-2}	corr. rate, μm year^{-1}	E_{corr}, mV	b_a, mV dec^{-1}	b_c, mV dec^{-1}	Z_{inh}, %
-	32.02	756	-191	62	-224	-
$6 \cdot 10^{-4}$	2.66	63	-172	174	-192	91.7
$8 \cdot 10^{-4}$	0.87	21	-257	121	-224	97.3
$1 \cdot 10^{-3}$	1.67	39	-180	146	-121	94.8
$1.2 \cdot 10^{-3}$	3.82	90	-185	195	-214	88.1

3.2. Polarization resistance determination

The optimum concentration of each examined inhibitor was also determined from polarization resistance measurements.

VpCI

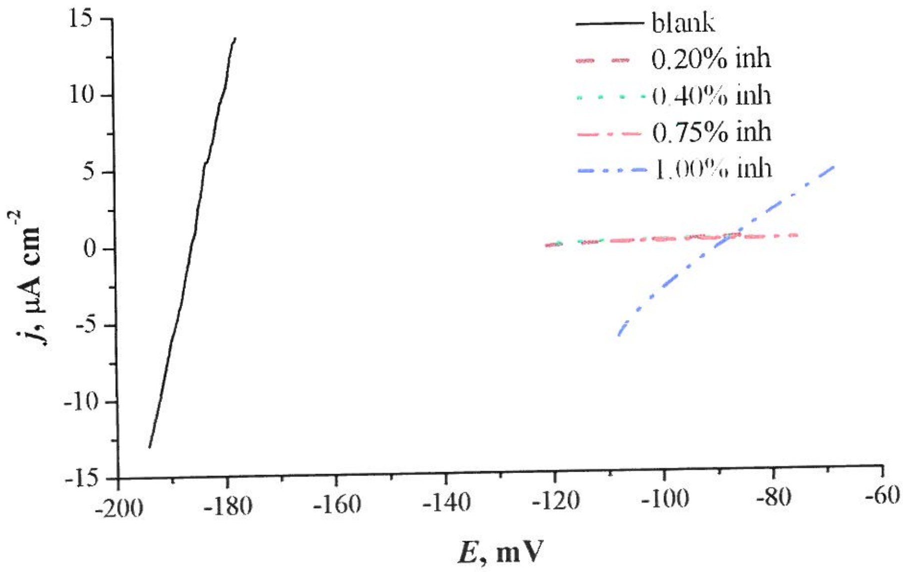

Figure 5. Polarization curves for bronze in artificial seawater without and with the addition of different concentrations of inhibitor VpCI

Corrosion parameters determined from the polarization curves recorded in narrow potential range are presented in Table V. It can be seen that the polarization resistance increases in the presence of VpCI and that it is the highest for the concentration that was found to be optimal by Tafel extrapolation method: 0.75 vol. % and the efficiency equals 99.7%.

TABLE V. Corrosion parameters for bronze in artificial seawater without and with the addition of different concentrations of inhibitor VpCI, obtained by polarization resistance measurements

c_{inh}, %	j_{corr}, μA cm^{-2}	corr. rate, μm year^{-1}	E_{corr}, mV	R_p, kΩ cm^2	Z_{inh}, %
-	36.98	873	-191	0.6	-
0.20	0.56	13	-104	79.1	98.5
0.40	0.31	7	-109	111.6	99.2
0.75	0.11	21	-97	195.8	99.7
1.00	12.88	304	-87	4.2	65.2

Polarization curves of bronze recorded in artificial seawater and in the presence of various concentrations of inhibitor PI are presented in Figure 6, while corrosion parameters obtained by polarization resistance determination are given in Table VI.

1-phenyl-4-methyl-imidazole (PI)

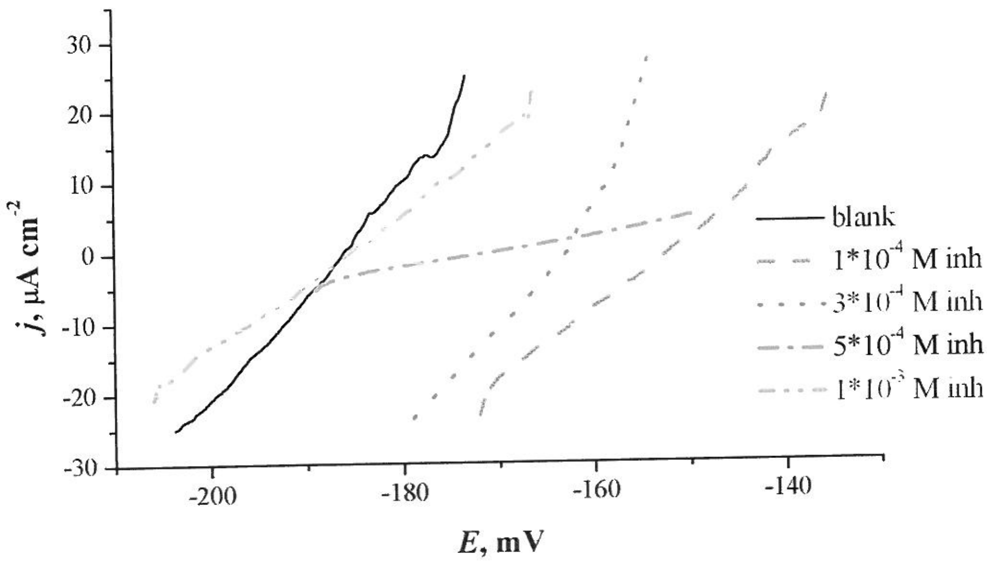

Figure 6. Polarization curves for bronze in artificial seawater without and with the addition of different concentrations of inhibitor 1-phenyl-4-methyl-imidazole (PI)

TABLE VI. Corrosion parameters for bronze in artificial seawater without and with the addition of different concentrations of inhibitor 1-phenyl-4-methyl-imidazole (PI), obtained by polarization resistance measurements

c_{inh}, mol dm^{-3}	j_{corr}, μA cm^{-2}	*corr. rate*, μm year^{-1}	E_{corr}, mV	R_p, kΩ cm^2	Z_{inh}, %
-	36.98	873	-191	0.6	-
$1\cdot10^{-4}$	17.26	408	-152	1.0	53.3
$3\cdot10^{-4}$	23.26	549	-162	0.6	37.1
$5\cdot10^{-4}$	4.98	118	-170	5.0	86.5
$1\cdot10^{-3}$	29.55	698	-185	1.0	20.1

The maximum efficiency of inhibitor PI was obtained at relatively low inhibitor concentration $5\cdot10^{-4}$ mol dm^{-3}.

benzotriazole (BTA)

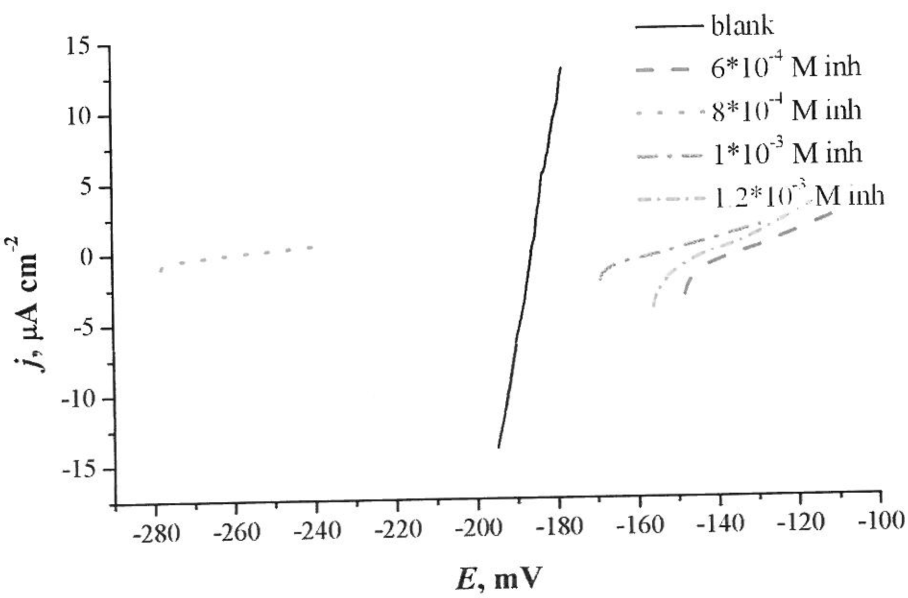

Figure 7. Polarization curves for bronze in artificial seawater without and with addition of different concentrations of inhibitor benzotriazole (BTA)

Polarization measurements performed in narrow potential range (Figure 7.) have confirmed that BTA provides the highest protection at concentration $8*10^{-4}$ mol dm^{-3}. From corrosion parameters given in Table VII it can be seen that the polarization resistance obtained for optimum BTA concentration is much higher than that observed in uninhibited solution, however polarization resistance obtained for optimum VpCI concentration (Table V) is 6 times higher. Therefore it may be concluded that examined sugar beet derivative (VpCI) is much better corrosion inhibitor for bronze in sea water than BTA.

TABLE VII. Corrosion parameters for bronze in artificial seawater without and with the addition of different concentration of inhibitor benzotriazole (BTA), obtained by polarization resistance measurements

c_{inh}, mol dm^{-3}	j_{corr}, μA cm^{-2}	*corr. rate*, μm $year^{-1}$	E_{corr}, mV	R_p, kΩ cm^2	Z_{inh}, %
-	36.98	873	-191	0.6	-
$6\cdot10^{-4}$	3.77	89	-131	10.2	89.8
$8\cdot10^{-4}$	0.97	23	-257	35.2	97.4
$1\cdot10^{-3}$	2.33	55	-150	12.3	93.7
$1.2\cdot10^{-3}$	4.12	97	-138	10.8	88.9

3.3. Electrochemical impedance spectroscopy (EIS)

EIS measurements were performed for the same inhibitor concentrations as used for polarization and Tafel extrapolation measurements.

VpCI

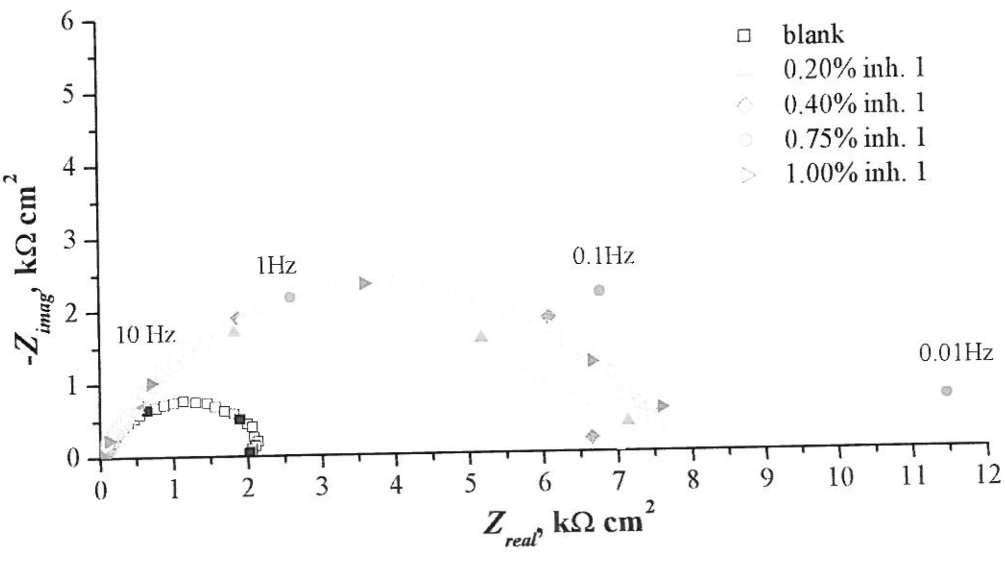

Figure 8. Nyquist impedance spectra for bronze in artifical seawater without and with the addition of different concentrations of inhibitor VpCI.

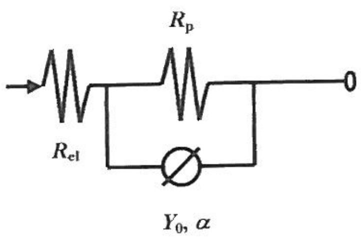

Figure 9. Equivalent electrical circuit representing studied system

EIS spectra can be represented by simple equivalent circuit given in Figure 9. R_{el} represents electrolyte resistance, R_p polarization resistance, Y_o constant phase element related to double layer capacitance while α is a coefficient representing the depressed feature in Nyquist diagram.

The EIS parameters obtained by fitting the experimental results for inhibitor VpCI to proposed model are given in Table VIII. They show that the polarization resistance significantly increases in the presence of inhibitor. The value of the constant phase element Y_0 that is related to double layer capacitance decreases in the presence of studied inhibitor and is the lowest for the optimum inhibitor concentration. Decrease of Y_o suggests the presence of adsorbed inhibitor on the bronze surface. It is also interesting to note relatively low α value from which it may be assumed that bronze surface is very heterogeneous.

TABLE VIII. Impedance parameters for bronze in artificial seawater without and with addition of different concentrations of inhibitor VpCI

c_{inh}, %	R_{el}, Ω cm^2	R_p, kΩ cm^2	$Y_0 \cdot 10^{-6}$, S·s^α cm^{-2}	α
-	6.6	2.16	196	0.77
0.20	4.9	7.35	100	0.63
0.40	4.8	9.95	68	0.65
0.75	5.0	15.02	44	0.68
1.00	5.0	8.09	95	0.34

Results obtained for VpCI are given in Figure 9. and Table VIII. The highest impedance was observed for 0.75% inhibitor concentration and it was nearly 15 kΩ cm^2 that is also the highest impedance exhibited by studied compounds. Therefore it may be concluded that inhibitor VpCI is the most effective among the examined compounds.

1-pheny- 4-methyl-imidazole (PI)

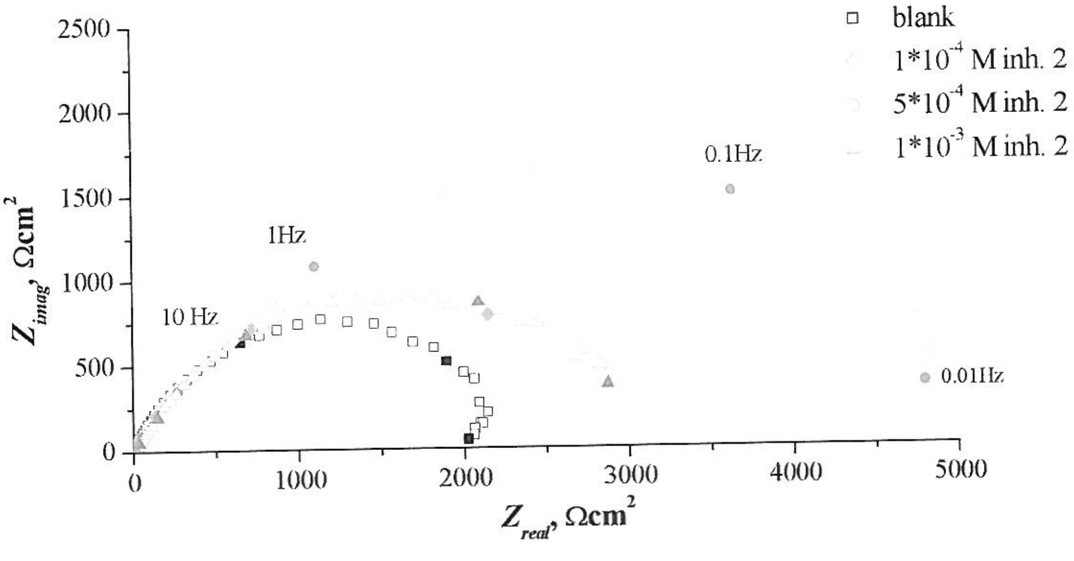

Figure 10. Nyquist impedance spectra for bronze in artificial seawater without and with addition of different concentrations of 1-phenyl-4-methyl-imidazole (PI)

Impedance spectra obtained for inhibitor PI are presented in Figure 10. The biggest diameter of impedance loop was observed for $5\cdot10^{-4}$ moldm^{-3} inhibitor concentration, the same as it was observed by dc methods.

TABLE IX. Impedance parameters for bronze in artificial seawater without and with the addition of different concentrations of inhibitor 1-phenyl-4-methyl-imidazole (PI)

c_{inh}, mol dm^{-3}	R_{el}, Ω cm^2	R_p, kΩ cm^2	$Y_0\cdot10^{-6}$, S·s^a cm^{-2}	a
-	6.6	2.162	196	0.77
$1\cdot10^{-4}$	5.8	2.887	201	0.73
$5\cdot10^{-4}$	5.7	4.983	128	0.71
$1\cdot10^{-3}$	5.6	3.015	233	0.69

Results obtained for BTA are given in Figure 11. and Table X. The highest polarization resistance was observed for optimum concentration ($8\cdot10^{-4}$ mol dm^{-3}) and it was about 9 kΩ cm^2. BTA did not exhibit significant influence on double layer capacitance values.

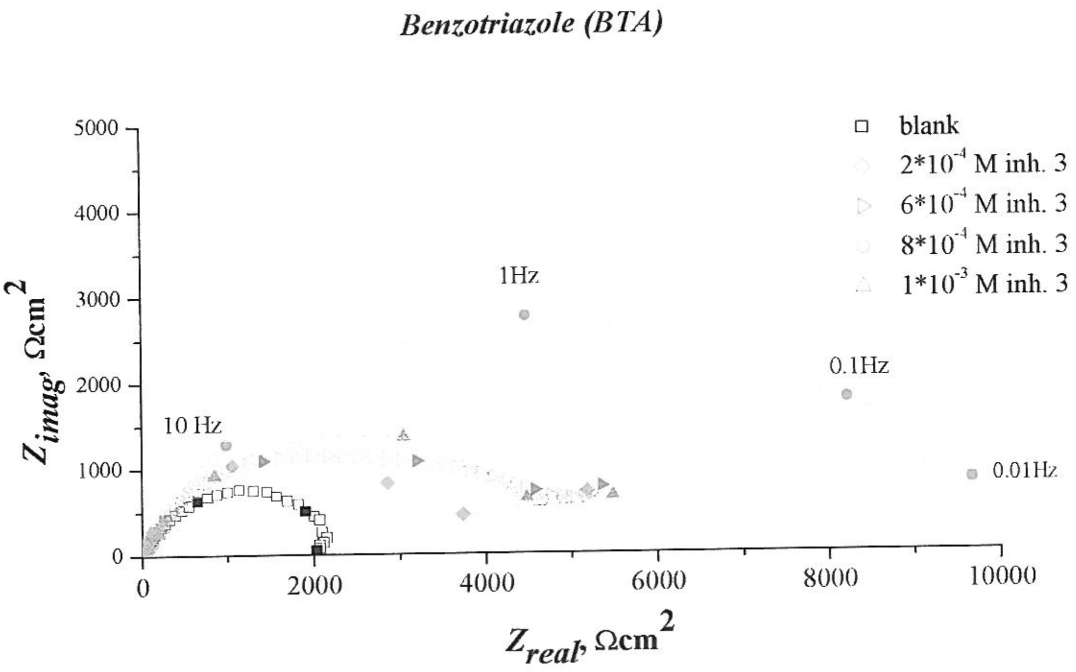

Figure 11. Nyquist impedance spectra for bronze in artificial seawater without and with addition of different concentrations of inhibitor BTA

TABLE X. Impedance parameters for bronze in artificial seawater without and with addition of different concentrations of inhibitor BTA

c_{inh}, mol dm^{-3}	R_{el}, Ω cm^2	R_p, kΩ cm^2	Y_0·10^{-6}, S·s^α cm^{-2}	α
-	6.6	2.162	196	0.77
$2\cdot10^{-4}$	6.6	3.648	180	0.82
$6\cdot10^{-4}$	5.6	4.332	180	0.75
$8\cdot10^{-4}$	5.1	8.944	260	0.73
$1\cdot10^{-3}$	5.1	4.983	410	0.67

4. Conclusion

The present study investigated corrosion of bronze in seawater and the effectiveness of the protection of bronze with environmentally friendly corrosion inhibitors, as possible replacement of benzotriazole.

Results obtained by polarization measurements showed that the corrosion rate decreases in the presence of each inhibitor. Study was performed for different concentrations of inhibitors. In the tested concentration interval, vapor phase corrosion inhibitor based on the sugar beets extracts showed the lowest rate of corrosion of 2 μm year^{-1} for concentration of 0.75%. The effectiveness of inhibitor in mentioned case is 99%. Inhibitor 1-phenyl-4-methyl imidazole showed the highest efficiency at concentration of $5\cdot10^{-4}$ moldm^{-3}. The rate of corrosion in this case was 129 μm year^{1},with inhibitor effectiveness of 83%. *BTA* was a control inhibitor. The highest efficiency of 97% for *BTA* was at concentrations $8\cdot10^{-4}$ moldm^{-3} and the corrosion rate in this case was 21 μm year^{-1}.

These results confirmed that in highly aggressive media like seawater benzotriazole can be replaced with environmentally friendly corrosion inhibitors (VpCI and PI) which provide the same or better corrosion protection to bronze.

Measurements performed by the use of electrochemical impedance spectroscopy also showed corrosion resistance improvement in the presence of studied inhibitors. Again, all inhibitors showed similar behavior as observed by dc methods. Considering all experimental methods used it may be concluded that VpCI is the most effective compound examined in this work.

Acknowledgements

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