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EVALUATION OF PHENOTHIAZINE AS ENVIRONMENTALLY FRIENDLY CORROSION INHIBITOR FOR BRONZE IN SYNTHETIC ACID RAIN

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ABSTRACT. Inhibition performance of phenothiazine as safe corrosion inhibitor for bronze in a solution containing Na_2SO_4 and $NaHCO_3$ (pH=5) that simulates an acid rain in an urban environment was investigated by potentiodynamic polarization and electrochemical impedance measurements. The results showed that phenothiazine is a fairly efficient inhibitor towards bronze corrosion, even when added in µM concentration range. The inhibition efficiency of phenothiazine increases with its concentration and attains a value higher than 91% at 150 µM concentration level. The adsorption of phenothiazine on bronze surface obeys the Langmuir's isotherm. Phenothiazine was proved to be a promising environmentally-safe alternative to the harmful corrosion inhibitors used for the protection of bronze against corrosion in aggressive media.

Key words: *bronze, corrosion, phenothiazine, electrochemical impedance spectroscopy, polarisation curve*

INTRODUCTION

The corrosion of copper and bronze in acidic media is a major problem affecting numerous sculptures, ornamental work materials and archaeological artefacts, but also industrial applications (battery connectors, distribution systems etc.) [1].

One of the most efficient alternatives to prevent bronze dissolution in aggressive media is the use of corrosion inhibitors. Nevertheless, many common corrosion inhibitors widely used to protect copper [2-4] and its alloys from corrosion [5-8], such as chromates [9], organic compounds containing heteroatoms with high electronic density (*i.e.* nitrogen, sulphur and oxygen) or those containing multiple aromatic bonds [10] are harmful substances and most of them cannot be biodegraded [11].

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Nowadays, the increasing consciousnesses of the health and ecological policies for the use of chemicals have changed the traditional approach of corrosion inhibition science [12]. Consequently, the utilization of these compounds has been limited by their degree of toxicity [13] and the current research focuses on the development of new “green” inhibitors, compounds having good inhibition efficiency, but low or zero risk of environmental pollution [8].

In this context, the present research aims to investigate the inhibition properties of phenothiazine on bronze corrosion in a solution containing Na_2SO_4 and $NaHCO_3$ (pH=5) that simulates an acid rain in urban environments. In small concentrations, phenothiazine is nor toxic, neither noxious towards human beings or the environment, is relatively cheap, easy to produce in high purity and is used in the antihistaminic drugs production [14]. Moreover, some derivatives of phenothiazine have been already reported as efficient corrosion inhibitors for copper-based alloys [15].

Electrochemical techniques, such as potentiodynamic polarization and electrochemical impedance spectroscopy measurements (EIS) were used to gain more information on the inhibition mechanism of phenothiazine on bronze corrosion.

RESULTS AND DISCUSSION

Potentiodynamic polarization measurements

Fig. 1 shows cathodic and anodic polarization scans recorded for bronze in 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$ (pH=5) solution at 25ºC, in the absence and presence of various concentrations of phenothiazine over the range 1 – 150 μM.

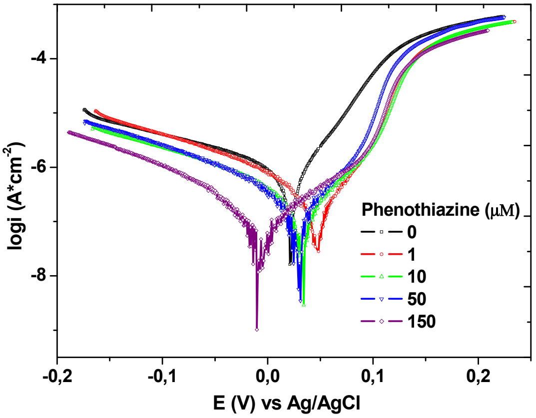


Figure. 1. Tafel polarization curves for bronze corrosion in Na_2SO_4/$NaHCO_3$ solution (pH 5) with various concentrations of phenothiazine. Scan rate: 10 mV/min.

From Fig. 1, it can be observed that both the anodic metal dissolution and oxygen reduction reactions are hindered when different concentrations of phenothiazine are added to the corrosive solution. A shift of the corrosion potential towards more positive values as compared to the E_{corr} value calculated for blank solution could be also observed in the presence of phenothiazine at concentrations below 100 μM. In the presence of higher concentration of phenothiazine (150 μM), the corrosion potential is negatively shifted.

The corrosion parameters derived from these curves, such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c and β_a) and corrosion current density (i_{corr}) are summarized in Table 1. The values of inhibition efficiency (IE) of the phenothiazine as a function of its concentration are also presented in Table 1.

The IE values were calculated according to the following equation:

$$IE = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \qquad [\%] \qquad (1)$$

where i^0_{corr} and i_{corr} are the values of the corrosion current densities in absence and in presence of phenothiazine, respectively.

Table 1. Corrosion parameters obtained from the polarization curves

Inhibitor	conc. (μM)	E_{corr} (mV/ Ag/AgCl)	i_{corr} (μA/cm^2)	- β_c (mV/dec)	β_a (mV/dec)	IE (%)
Blank	0	22	0.66	172	46	-
Phenothiazine	1	47	0.22	81	55	66.6
	10	34	0.17	89	60	74.2
	50	31	0.11	65	43	83.3
	150	-10	0.06	54	71	90.9

The values of the corrosion current density decrease with increasing phenothiazine concentration and the inhibition efficiency attains the highest value of 90.9% in the presence of 150 μM phenothiazine.

The presence of the different concentrations of phenothiazine in the corrosive media change significantly the cathodic (β_c) Tafel slopes. In the case of anodic (β_a) Tafel slope, the values obtained in the presence of different concentrations of phenothiazine are not significantly different from the value obtained in the absence of phenothiazine, which means that phenothiazine has a stronger effect on the cathodic oxygen reduction process, probably by blocking the O_2 access to the bronze surface.

Electrochemical impedance spectroscopy measurements

Fig. 2 shows the impedance spectra of bronze electrode immersed in 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$ (pH 5) solution, in the absence and in the presence of various concentrations of phenothiazine (1 to 150 μM), represented as Nyquist and Bode plots.

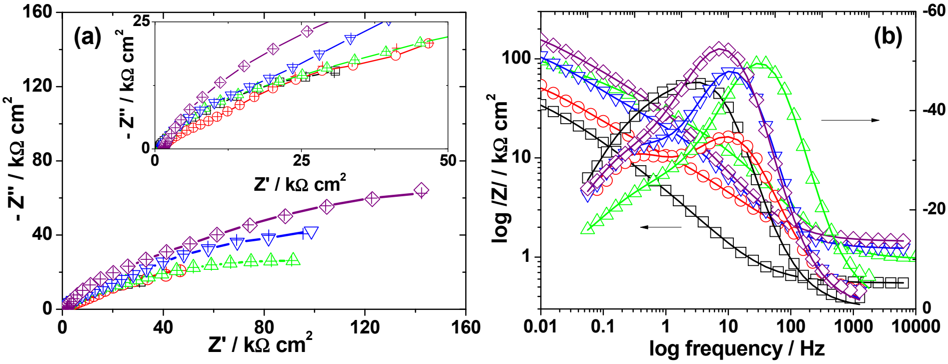


Figure 2. Nyquist (a) and Bode (b) plots of bronze electrode in $Na_2SO_4/NaHCO_3$ (pH 5) solution, in the absence and in the presence of different concentrations of phenothiazine (μM): (□) 0; (○)1; (Δ); 10; (∇) 50; (◊) 150. The symbol (—+—) corresponds to the fitted data.

It can be noticed that all experimental plots have a depressed semicircular shape in the complex impedance plane, with the centre under the real axis (Fig. 2). This behaviour is typical for solid metal electrodes that show frequency dispersion of the impedance data and could be attributed to roughness and other inhomogeneities of the solid surface [16]. Consequently, constant phase elements (CPEs) represented by the terms, Q and n are often used nowadays instead of pure capacitances to represent the depressed features of the capacitive loops.

The impedance of the CPE is given by [17]:

$$Q = Z_{CPE(\omega)} = [C(j\omega)^{n}]^{-1} \tag{2}$$

where j is an imaginary unit and ω is the angular frequency in rad s^{-1}.

The equivalent circuit used for fitting the experimental data is presented in Fig. 3, where R_e corresponds to the electrolyte resistance, the parameter R_{ct} coupled with Q_d describe the charge transfer process at the electrolyte/bronze interface, while the low frequency elements, R_F and Q_F correspond to an oxidation-reduction process taking place at the electrode surface, probable involving the corrosion products layers accumulated at the interface. A similar circuit was formerly used by K. Marusic *et al.* [18] to explain bronze corrosion in the presence of 4-methyl-1-p-tolylimidazole.

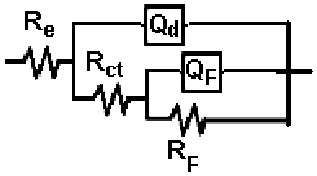


Figure 3. Equivalent electrical circuit used to reproduce the experimental data

The good agreement between the experimental and the calculated values of the impedance from Fig. 2 indicates that (2RQ) equivalent electrical circuit properly reproduce the experimental data corresponding to the bronze corrosion in weak acidic solution, in the absence and in the presence of the phenothiazine, respectively.

The values of the pseudo-capacitances associated with the CPEs were recalculated using the equation [17]:

$$C = \left(R^{1-n} Q\right)^{1/n} \tag{3}$$

The variations of the calculated R-C parameters as a function of the organic inhibitor concentration are illustrated in Fig. 4.

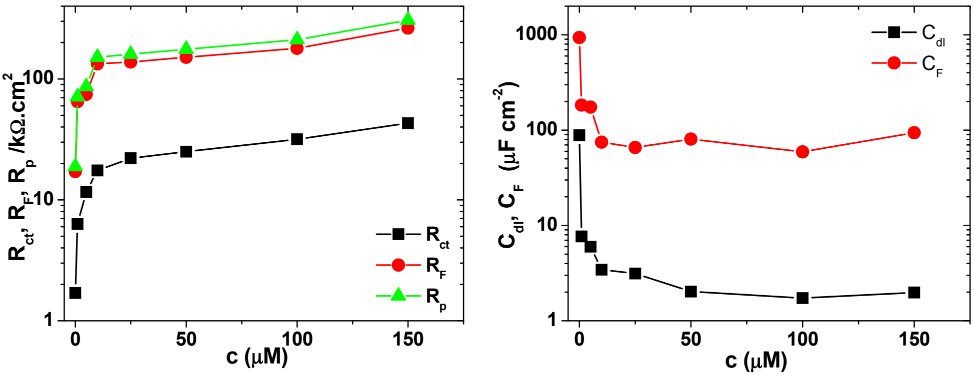


Figure 4. Calculated EIS data for bronze corrosion in $Na_2SO_4/NaHCO_3$ (pH 5) solution, without and with the addition of different concentrations of phenothiazine

In the blank solution, the calculated value of capacitance C_{dl} is 88.3 μF cm^{-2}, plausible for a double layer capacitance, thus validating the model used for experimental data simulation. In the presence of phenothiazine, the C_{dl} values decrease as a consequence of inhibitor adsorption on the bronze surface leading to a smaller area of the electrode directly in contact with the electrolyte under the corrosion product layer or to a less conductive nature of this film.

The values of the charge transfer resistance, R_{ct}, significantly increase with the organic compound concentration, being related to the corrosion protection effect of the phenothiazine molecule. This effect is enhanced upon increasing phenothiazine concentration.

With increasing the phenothiazine concentration, the faradaic resistance R_F values increase, while simultaneously the C_F decreases. Consequently, it was assumed that the adsorption of the organic compounds on the bronze surface hinders the formation of the corrosion products and stabilizes the species covering the electrode, which became less susceptible to redox processes and confer better protection to the electrodic surface [15].

It is common knowledge that, in the presence of a redox process taking place at the bronze surface, the parameter which is closer related to the corrosion rate is the polarisation resistance, R_p.

Consequently, the R_p values, calculated as the sum of the two resistances (R_{ct} and R_F) were used to determine the inhibition efficiency of phenothiazine, as a function of their concentration, according to following equation:

$$IE = \frac{R_p - R_p^0}{R_p} \tag{4}$$

where R_p^0 and R_p are the polarisation resistances in electrolytes without and with inhibitor, respectively.

As it can be seen in Table 2, the inhibition efficiency values, calculated from ac impedance results show the same trend as those estimated from the polarization measurements. In the investigated experimental conditions, the maximum IE value (93.8 %) was obtained in the presence of 150 μM phenothiazine.

Table 2. Corrosion parameters obtained from the impedance measurements

Inhibitor	**c (μM)**	**IE (%)**	**θ**
Blank	0	-	-
Phenothiazine	1	73.5	0.731
	5	78.2	0.854
	10	87.5	0.903
	25	88.3	0.923
	50	89.3	0.932
	100	91.1	0.946
	150	93.8	0.961

Adsorption isotherm

Basic information on the interaction between the inhibitor and the metal surface can be provided by the adsorption isotherm.

The experimental data obtained from EIS measurements were used to determine the adsorption characteristics of phenothiazine on bronze in $Na_2SO_4/NaHCO_3$ (pH 5) solution.

The values of the surface coverage degree, θ for different inhibitor concentrations, calculated according to the equation (5) are presented in Table 2.

$$\theta = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \tag{5}$$

where R_{ct}^0 and R_{ct} are the charge transfer resistances in electrolytes without and with inhibitor, respectively.

In the investigated conditions, the plots of the experimental θ values to various adsorption isotherms (Langmuir, Frumkin and Temkin) showed that the adsorption of phenothiazine on bronze surface follows the Langmuir isotherm (Fig. 5), according to the following equation:

$$\frac{c}{\theta} = \frac{1}{K} + c \tag{6}$$

where *K* is the adsorption equilibrium constant, *c* represents the phenothiazine concentration expressed in molar units.

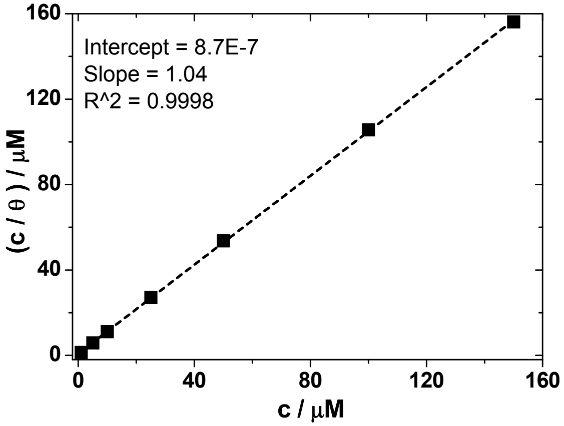


Figure 5. Langmuir adsorption isotherm of phenothiazine on the bronze surface in $Na_2SO_4/NaHCO_3$ (pH 5) solution, at 25^0 C

The plot of c/θ versus c yields to a straight line with slope close to unit (Fig. 5) confirming that the adsorption of phenothiazine on bronze surface obeys the Langmuir isotherm.

The standard free enthalpy of adsorption ΔG^0_{ads} was determined from the adsorption equilibrium constant, *K* according to the following equation [19]:

$$\Delta G^0_{ads} = -RT\ln(55.5K) \quad (7)$$

where 55.55 represents the molar concentration of water in solution (mol dm^{-3}), *R* is the gas constant and *T* is the absolute temperature.

The calculated ΔG^0_{ads} value of -44.5 kJ/mol suggests that the adsorption of phenothiazine on bronze is spontaneous and occurs mainly by chemisorption.

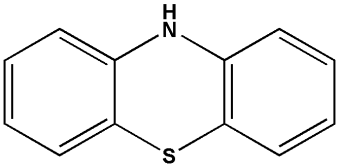
CONCLUSIONS

The ability of phenothiazine to hinder bronze corrosion in a simulated acid rain was examined in order to understand the processes leading to the inhibition of metal dissolution. Both potentiodynamic polarization and impedance spectroscopy studies demonstrate the inhibiting properties of this molecule, even when added at µM concentration range. The protective effectiveness of phenothiazine on bronze corrosion increases with increasing the inhibitor concentration and reaches a value higher than 91% at a concentration level as low as 150 µM. Similarly to other molecules containing N and S in their structure, the inhibitive action of phenothiazine is a consequence of its adsorption on the bronze surface forming a blocking barrier against corrosion. The adsorption process of phenothiazine follows the Langmuir isotherm.

The environmentally friendly properties of phenothiazine make it favourable to be used in practice, replacing some toxic corrosion inhibitors, in accordance with the ecological policies for the use of chemicals.

EXPERIMENTAL

The molecular structure of the phenothiazine is presented in Scheme 1.



Scheme 1. Molecular structure of phenothiazine

The corrosive medium employed was an aqueous aerated solution of 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$, acidified to pH=5 by addition of dilute H_2SO_4, that was prepared from analytical grade reagents and distilled water. This solution simulates an acidic rain in urban environment [15]. The presence of sulphate simulates the pollution by sulphur dioxide frequently induced by petroleum nowadays and coal at ancient time [18]. The presence of carbonate ions is due to the natural composition of air, *i.e.* 0.033% [18]. The working electrode used in this study was prepared from a cylindrical bar of bronze (Cu-94.03, Sn-3.31, Pb-0.24, Zn-1.44, Ni-0.25, Fe-0.22, Si-0.51, at. %). The electrode was sealed with epoxy resin and only its cross section (0.28 cm^2) was allowed to contact the aggressive solutions. Prior to each experiment, the electrode was mechanically ground using successive grades of silicon carbide paper up to grade 2400, and then rinsed with distilled water and finally degreased with ethanol.

A three-electrode cell consisting of a bronze working electrode, a platinum counter electrode and a silver–silver chloride (Ag|AgCl, KCl_{sat}) electrode as reference electrode was used for the measurements. All electrochemical experiments were performed at room temperature without stirring, using a PAR model 2273 potentiostat controlled by a PC computer.

Before each experiment, the bronze electrode was left at the open circuit potential for 1 hour in the corrosive solution to establish the steady state condition. After measuring the open circuit potential, polarization curves were recorded at constant sweep rate of 10 mV/min, in the potential range from -200 to +200 mV with respect to the open circuit potential.

Electrochemical impedance spectroscopy measurements (EIS) were carried out at the open circuit potential after 1 hour immersion of the bronze electrode in the corrosive medium. The impedance spectra were acquired in the frequency range 10 kHz to 10 mHz at 10 points per hertz decade with an AC voltage amplitude of ± 10 mV. The impedance data were interpreted on the basis of equivalent electrical circuits, using the ZSimpWin V3.21 software for fitting the experimental data.

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