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EVALUATION OF NATURAL HONEY AS CORROSION INHIBIT OR FOR BRONZE IN WEAKLY ACIDIC SOLUTION

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Abstract

Natural honey was tested as a corrosion inhibitor for bronze in a simulated acid rain solution as Na2SO4and NaHCO3 (pH 5).Electrochemical investigations (potentiodynamic polarization and impedance measurements) showed that honey exert a protective effect against corrosion bronze and, in some cases inhibiting its effectiveness exceeds 93% at concentration level as low as 500ppm. Potentiodynamic polarization method indicates that honey acts mainly as a mixed-type inhibitor with predominantly control of thecathodic reaction. The presence of honey significantly decreases the values of corrosion current density. Electrochemical impedance spectroscopy shows that the inhibition efficiency increases with the increases of honey concentration.

Key words: *Corrosion inhibitors; Natural honey; Electrochemical impedance spectroscopy; Potentiodynamic polarization*

INTRODUCTION

Nowadays, air pollution strongly contributes to the corrosion of materials (Morselli et al., 2004). Copper and copper-based alloys are widely used in various structural, architectural, electrical and electronic applications. In spite of the fact that copper is a relatively noble metal, it can suffer severe corrosion in oxygen-containing environments. Since copper and its alloys are not stable in oxygen-containing electrolytes substantial improvement in their passivity can be achieved by using corrosion inhibitors (Bostan et al., 2012).

One of the most effective alternatives for the protection of metallic surfaces against corrosion is the use of corrosion inhibitors. Usually, organic compounds that exert significant anticorrosive proprietiespossess heteroatoms such as N, S or O and conjugated multiple bonds in their molecules. In many cases, the synthesis of these compounds is expensive, and most of them are toxic for human beings and hazardous for the environment. Therefore, in line with the environment protection regulations, the new trend in industry is nowadays orientated toward finding new ecologically harmless, green corrosion inhibitors with low risk of pollution. Recently, there is an increased interest in employing naturally occurring substances and extracts which fulfil these requirements to be used as effective corrosion inhibitors (Radojcic et al., 2008).

In the last years, various works focused on the investigation of the anticorrosive properties of natural honey on aluminum, steel, tin, Al–Mg–Si alloy in various aggressive media (Radojcic et al., 2008), (Rosliza et al.,2010). Honey is a natural result that is processed by bees from the nectar of flowers or parts of plants (Gapsari et al.,2015). It containing a range of nutritiously important complementary elements: saccharides, organic acids, amino acids, polyphenols, mineral matter, colors, aromatic substances, trace amounts of fat, and some valuable but unstable compounds such as enzymes, substances of hormonal character, some vitamins and a few minor compounds. It is considered as part of traditional medicine being effective in gastrointestinal disorders, in healing of wounds and burns, and as an antimicrobial agent (Radojcic et al., 2008).

The purpose of this work is to investigate for the first time the inhibition properties of honey on bronze corrosion in a solution containing

Na_2SO_4 and $NaHCO_3$ (pH 5) that simulates acid rain in an urban environment. Electrochemical techniques, such as potentio dynamic polarization and electrochemical impedance spectroscopy measurements (EIS) were used to elucidate the inhibition properties of honey on bronze corrosion (Gapsari et al.,2015).

MATERIALS AND METHODS

Electrochemical measurements

A three-electrode cell was used for the electrochemical experiments. The counter-electrode was a large platinum grid and Calomel electrod, KCl_{sat} was used as reference electrode. An electrode made of bronze (Cu-94.03%, Sn-3.31%, Pb-0.24%, Zn-1.44%, Ni-0.25, Fe-0.22, S-0.51, at.%) was used as working electrode.

In order to avoid the electrolyte infiltration, the lateral part of the bronze rod was firstly protected by a cataphoretic paint layer, cured at 150 LC for 30 min. The rod specimen was embedded in epoxy resin (Buhler, EpoxycureTM) with an exposed area of 0.283 cm^2. Prior to measurements, the working electrode was a mechanically ground using successive grade of silicon carbide paper up to grade 2400, and then rinsed thoroughly with distilled water and ethanol.

The bronze sample was transferred into the electrochemical cell and the measurements were carried out in an aqueous solution of 0.2 g/l Na_2SO_4 + 0.2 g/l $NaHCO_3$, acidified to pH 5 by addition of dilute H_2SO_4. Appropriate weighted amounts of natural honey were dissolved in the corrosive electrolyte, in order to obtain various concentrations between 50 to 1000 ppm.

Electrochemical experiments were performed at room temperature, 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 h in the corrosive solution.Polarization curves were recorded at constant sweep rate of 10 mV/min in a potential range of ±200 mV vs. open circuit potential.

The corrosion inhibition efficiency (IE) was calculated from the polarization curves according to following equation:

$$IE = \frac{i\ corr0 - i\ corr}{i\ corr0} * 100(\%)$$

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

Electrochemical impedance spectroscopy measurements were carried out at the open circuit potential after 1 h immersion of the bronze electrode in the corrosive medium. The impedance spectra were acquired in the frequency range 10 kHz to 10 mHzat 5 points per hertz decade with AC voltage amplitude of ± 10 mV.

The percentage of inhibition efficiency (IE) was calculated from the polarization resistance values determined from the linear polarization measurements and from the electrochemical impedance spectra, according to the following equations:

$$IE = \frac{Rp - R0p}{Rp} * 100 \quad (\%)$$

Where R_p and R^0_p are the polarization resistances in electrolytes with and without inhibitors, respectively.

RESULTS AND DISCUSSIONS

Potential dynamic polarization measurements

Fig. 1 shows representative Tafel polarization curves for bronze immersed in 0.2 g/l Na_2SO_4 + 0.2 g/l $NaHCO_3$ (pH 5) solution at in the absence and presence of different concentrations of honey.

Electrochemical kinetic parameters, such as corrosion potential (Ecorr), cathodic and anodic Tafel slopes (βc andβ) and corrosion current density (i_{cor}r) were estimated by extrapolation of the Tafel lines and are presented in Table 1. The inhibition efficiencies (IE) of the honey calculated according to Eq. (1) are also given in Table 1. The polarisation resistance (Rp) values (Table 1) were determined as the slopes of the linear polarization curves recorded after 1 h immersion of the bronze in the corrosive solution.

As can be seen in Figure 1, both the cathodic and anodic branches are influenced by the presence of honey and its effect depends on the inhibitor' concentration in the electrolyte. The addition of honey in the corrosive solution leads to an important decreases of cathodic current densities as compared to the blank solution, in the whole applied potential range. A small decrease of the anodic current densities in the presence of honey could be also observed in Figure 1. However, disregarding its concentration, honey appears to have a more noticeable inhibiting effect on the cathodic process than on the anodic one, as attested by the shift of the corrosion potential towards more negative values. These results shows that honey is able to inhibit corrosion process mainly retarding the oxygen evolution reaction and increasing the charge transfer resistance of the anodic dissolution of copper.

The values of the inhibition efficiency presented in Table 1 confirm that honey has inhibiting properties on bronze corrosion. A possible explanation for their inhibiting effect could be found in the ability of the organic molecules from honey to absorb on electrode and to form a protective layer on the bronze surface. As expected, the inhibition efficiency of honey increases with its concentration reaching a maximum value of 89.58% for a concentration of 500 ppm. Nevertheless, a further increase of the honey concentration leads to a decrease of its protective effectiveness, probably due to the saturation of the bronze surface with inhibitor molecules at a certain concentration.

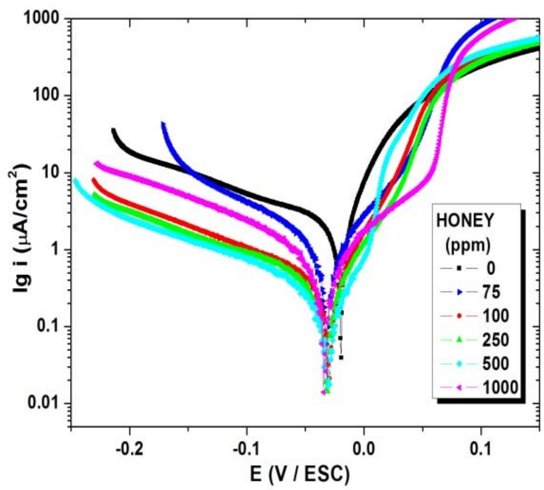

Figure 1.The polarization curves (Tafel curves) for bronze in $Na_2SO_4/NaHCO_3$ (pH 5) solution without and with various concentrations of honey

Table 1. Corrosion parameters obtained from the polarization curves

Concentration honey (ppm)	E_{cor} (mV/ESC)	i_{cor} (μA/cm²)	V_{cor} (m²/an)	$\lvert\beta_c\rvert$ (mV/dec)	β_a (mV)	IE (%)
0	-19.62	2.88	0.75	384.39	36.41	-
75	-29.02	0.41	0.11	174.62	41.79	85.76
100	-33.58	0.39	0.10	217.14	114.72	86.45
250	-30.41	0.34	0.89	126.95	63.82	88.19
500	-30.26	0.30	0.79	165.69	59.03	89.58
1000	-31.83	0.52	0.13	244.56	62.08	81.94

Electrochemical impedance spectroscopy

The corrosion behavior of bronze after 1 h immersion in the corrosive solutions without and with various concentrations of honey was further investigated by electro-chemical impedance spectroscopy (EIS). The measurements were conducted at the opencircuit potentials and the obtained Nyquistdiagram are depicted in Figure 2.

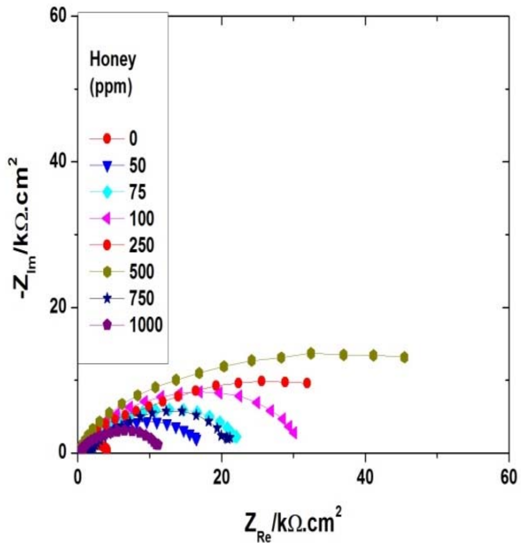

Figure 2. Nyquist impedance diagram of bronze electrode in $Na_2SO_4/NaHCO_3$ (pH 5) solution without and with various concentrations of honey.

Bronze impedance response was changed after the addition of honey in the corrosive solution; a significant increase of the impedance values at the lowest frequency (polarization resistance) could be observed in the presence of honey.

Table 2. Polarization resistance corresponding to bronze corrosion in $Na_2SO_4/NaHCO_3$ (pH 5) solution obtained in the absence and in the presence of various concentrations of honey determined from the impedance diagram

Concentration of honey (ppm)	**Rp ($k\Omega cm^2$)**	**IE (%)**
0	4.16	-
25	7.8	46.62
50	22.8	81.74
75	30.00	86.12
100	34.00	87.75
250	44.00	90.53
500	61.20	93.19
750	24.80	83.21
1000	12.50	66.69

The data in Table 2 show that the polarization resistances are relatively high in the presence of honey and their values increase with increasing honey concentration, which suggests that the layer covering the bronzesurface in the presence of honey is more protective than in its absence.The values of Rp and inhibition efficiency increase when honey was added to the blank solution, indicating a marked anticorrosion effect of this natural compound on bronze dissolution.This effect is enhanced upon increasing the honey concentration, suggesting that the protective effect of the inhibitors is due most likely to decreases of the surface area in contact with the corrosive solution. The highest inhibition efficiency of honey reaches the value of 93.19%, at a concentration of 500 ppm. Further increase in honey concentration leads to a slight decrease of IE values, in agreement with the results from measurements of polarization and could be a consequence of damage or dissolution of the layer adsorbed on the surface of bronze.

CONCLUSIONS

In this work, the anticorrosive proprieties of the natural honey were investigated in a solution containing Na_2SO_4 and $NaHCO_3$ (pH = 5) simulating acid rain in urban areas, by electrochemical methods. The preliminary results showed that honey is afairly efficient inhibitor towards bronze corrosion in weak acidic solution. In the investigated experimental conditions, the inhibition efficiency of honey increases with increasing its concentrations in the corrosive solution up to the optimum value of 500 ppm. An adherent layer of organic molecules adsorbed on bronze surface is responsible for the protective effect of the investigated compound.

Concluding it could be assessed that the environmentally friendly properties of honey and its low price make it a suitable candidate to be used in practice, replacing some toxic inhibitors, in accordance with the new ecological policies for the use of chemicals.

REFERENCES

L. Morselli, E. Bernardi, C. Chiavari, G. Brunoro, 2004,Corrosion of 85-5-5-5 bronze in natural and synthetic acid rain, Appl. Phys. A 79, 363–367

R. Bostan, S. Varvara, L. Gaina, L. M. Muresan, 2012, Evaluation of some phenothiazine derivatives as corrosion inhibitors for bronze in weakly acidic solution, Corrosion Science 63, 275–286

I. Radojcic, K. Berkovic, S. Kovac, J. Vorkapic-Furac, 2008, Natural honey and black radish juice as tin corrosion inhibitors, Corrosion Science 50, 1498-1504.

R. Rosliza, W. B. Wan Nik, S. Izman, Y. Prawoto, 2010, Anti-corrosive properties of natural honey on Al-Mg-Si alloy in seawater, Current Applied Physics 10, 923-929.

F. Gapsari, R. Soenoko, A. Suprapto, W.Suprapto, Bee Wax Propolis Extract as Eco-Friendly Corrosion Inhibitors for 304SS in Sulfuric Acid, International Journal of Corrosion Volume 2015, 10 pages.