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Corrosion Inhibition Action of Sulfamethoxazole for Brass in Acidic Media

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The corrosion inhibition action of sulfamethoxazole (SMX) on aesthetical brass has been investigated in synthetic acidic rainwater by means of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), optical microscopy, scanning electron microcopy (SEM) and Fourier Transformed Infrared spectroscopy (FT-IR). It was found that SMX inhibits the corrosion of the brass and the inhibition efficiency increased with increasing concentration. Maximum inhibition efficiency of about 84% has been obtained at the higher concentration of SMX in the synthetic acidic rainwater. Long time immersion test showed that the inhibition efficiency increases with immersion time as indicated the increase of total impedance. Surface characterization performed by FT-IR, optical and SEM analyzes allowed to establish that SMX acts as inhibitor by forming protective adsorbed layer.

Keywords: brass, sulfamethoxazole, corrosion inhibition, electrochemical impedance spectroscopy

1. INTRODUCTION

Copper and copper alloys have found wide application in a broad spectrum of industries, architecture and cultural objects. But when exposed in humid atmosphere, copper and copper alloys corrode with formation of oxides layers (patina). However, these patinas have a tendency for degradation when exposed to polluted atmosphere. Corrosion and corrosion protection play an important role in economies, cultural heritage protection and public safety. Chemical inhibitors have been used for metal corrosion protection and have been widely investigated [1-8]. The inhibiting effect of these inhibitors is attributed to their adsorption at the metal/electrolyte interface. The most effective and efficient inhibitors are compounds that have π bonds, heteroatoms (N, S, P, O) and some inorganic compounds such as chromate, dichromates, nitrites and so on [9-11]. Unfortunately, many of the corrosion inhibitors till used today are health hazards and/or cause environmental damages.

In the past two decades, the research in the field of corrosion inhibitors has been focused toward the goal of having effective non-toxic molecules with low or zero environmental impact. In recent years, researchers have paid attention on the use of drugs as corrosion inhibitors. In the literature, several authors have reported the influence of drugs on the metals corrosion in various media [12-17]. Sulfamethoxazole is a sulfa drug, derivative of sulfanilamide, which is widely used for the cure of bacterial infection in humans. It is most often used as part of a synergistic combination with trimethoprim in a 5:1 ratio in co-trimoxazole. SMX is commonly used as an agent to treat urinary tract infections. In addition, it can be used as an alternative to amoxicillin-based antibiotics to treat sinusitis. It can also be used to treat toxoplasmosis [18].

In this investigation, we used pure product of sulfamethoxazole purchased from Aldrich as corrosion inhibitor. This choice is based on the following reasons; it has a large number of functional adsorption centers such as $–NH_2$ group, $–SO_2–NH–$ group, O and N heteroatoms and aromatic rings. The present paper explore the use of SMX as a safe, low environment impact corrosion inhibitor for brass in synthetic acid rainwater using potentiodynamic polarization, electrochemical impedance spectroscopy. The effect of concentration on the corrosion inhibition process were thoroughly assessed and discussed. The electrochemical parameters governing the inhibition process were also calculated and discussed.

2. EXPERIMENTAL DETAILS

2.1. Material

Commercially Cu/Zn (70/30) brass was used in this study. The samples ($5.0 \times 3.0 \times 0.8$ cm^3) were polished with SiC abrasive papers 400, 600, 800 up to 1200 grit respectively, degreased with ethanol, etched for 10 min in acetone and then rinsed with distilled water and dried at room temperature before use for the corrosion tests. For each test, freshly polished sample were used.

2.2. Test solutions

All tests were performed in synthetic acidic rainwater solution: 0.2g.L^{-1} Na_2SO_4 + 0.2g.L^{-1} $NaNO_3$ + 0.2 g.L^{-1} $NaHCO_3$; pH =4. The pH of the solution was adjusted with sulfuric acid. This solution was used as blank solution and with various concentration of the inhibitor which molecular structure is given in Figure 1.

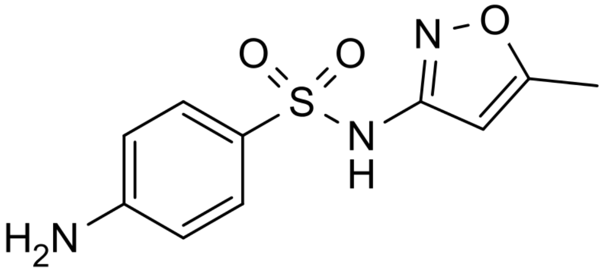

Figure 1. Structure of sulphamethoxazole[4-amino-N-(5-methyl-1,2-oxazol-3-yl)benzenesulfonamide]

The concentrations of inhibitor are ranging from 10^{-5} M to 10^{-3} M. All the test solutions were prepared with analytical-grade chemical reagents and distilled water.

2.3. Electrochemical measurements

A conventional three-electrode cell was used for the electrochemical tests. The working electrode was polished brass sample with surface area of $1cm^2$ exposed to electrolyte. The counter electrode was a platinum electrode; a saturated Ag/AgCl (+ 0.198 V vs. SHE) electrode was used as reference. All presented potential data were referred to this electrode. The cell was placed in a Faraday cage in order to minimize the noise level.

Potentiodynamic polarization measurements were performed using a PAR potentiostat 273A, after 1 hour of immersion, by polarizing the working electrode from an initial potential of -300 mV versus the open circuit up to 500 mV versus the reference. A scan rate of 2 mV/s was used.

The impedance measurements were carried out over frequencies ranging from 100 kHz to 10 mHz, at open circuit potential. The amplitude was 10 mV rms. The spectra were acquired by using a PAR potentiostat 273A coupled with a Solartron 1255 frequency response analyzer. In order to evaluate the inhibition effect over time, the impedance measurement was performed in time, leaving the sample immersed in the electrolyte. The impedance parameters were calculated by fitting the experimental results to an equivalent circuit using ZSimpwin 3.50 software.

2.4. Surface characterizations

FT-IR analysis was done on the thin adsorption layer formed on the brass surface, after 1 day immersion in the solution containing 10^{-3} M of SMX, which was cleaned with distilled water and dried with cold air bluster. The analyses were performed, with a VARIAN 4100 spectrometer, in an attenuated reflectance mode on diamond single reflection, in wavelength range from 4000 to 400 cm^{-1}. WIN-IR software from GALACTIC industries was used to analyze the spectrum peak. The brass surface morphologies before and after contact with SMX were observed by using scanning electron microscopy, with Philips XL30 microscope coupled with energy dispersive spectrometer (EDS).

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic results

The potentiodynamic polarization curves of the brass in blank solution and in the solutions containing different concentrations of SMX are presented in Figure 2. In the blank electrolyte, maximum corrosion current densities with average value of 1×10^3 µA.cm^{-2} were observed at the anodic domain when no inhibitor molecule was added. It is evident that in the presence of the inhibitor, the anodic current densities were significantly reduced from 1×10^3 µA.cm^{-2} to 86 µA.cm^{-2} at the optimal concentration of inhibitor; the current densities decrease with increasing concentration of the inhibitor. The cathodic branches display a limiting diffusion current due to the reduction of hydrogen according to the following equation [19].

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad \text{[eq.1]}$$

Thus, the cathodic process is controlled by concentration polarization rather than activation polarization. Nevertheless, both anodic and cathodic branches can be extrapolated to the corrosion potential E_{corr} to give the corrosion current i_{corr}. The data in the Tafel region (-0.2 to +0.2 V vs corrosion potential) have been fitted to evaluate the kinetic parameters.

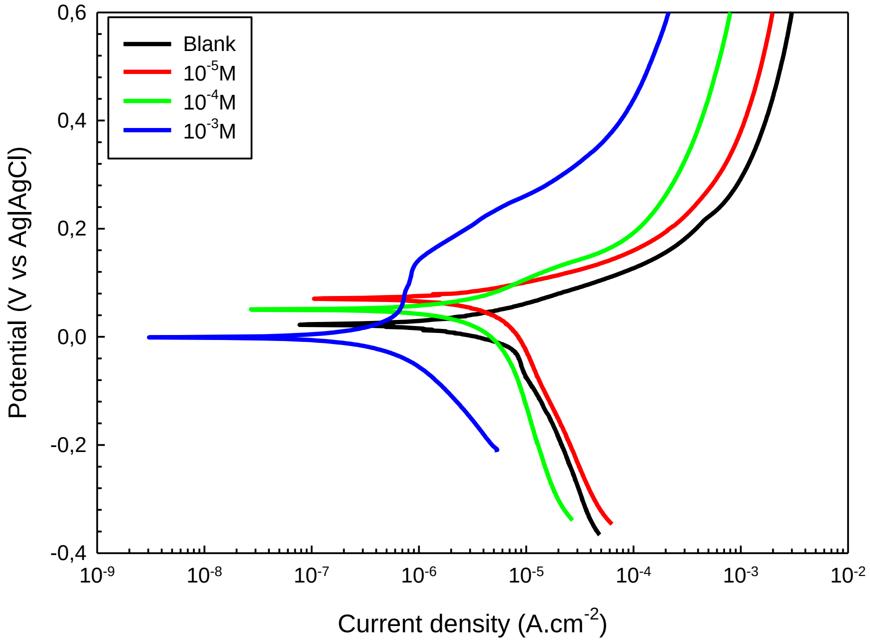

Figure 2. Potentiodynamic polarization curves of the brass in blank acid rain and presence of different concentrations of inhibitor

The linear Tafel segments of the anodic and cathodic curve were extrapolated to corrosion potential for obtaining the corrosion current (i_{corr}) values and then, the inhibition efficiency was evaluated from the obtained i_{corr} values according to the following equation

$$IE(\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \qquad \text{[eq.2]}$$

where i_{corr} and i'_{corr} are the corrosion current values without and with the addition of various concentration of SMX. The corrosion kinetic parameters derived from the polarization curves are reported on Table 1. From the table, it is clear that the addition of SMX in the concentration range 10^{-5}-10^{-3} M decrease the corrosion rate of the brass.

Table 1. Electrochemical parameters derived from the polarization curves

Concentration	E_{corr} (mV)	I_{corr} ($A.cm^{-2}$)	βa (mV)	βc (mV)	IE (%)
Blank	23 mV	2.88×10^{-6}	107.16	246.70	–
10^{-5}M	7 mV	8.45×10^{-7}	96.47	242.68	70.69
10^{-4}M	50 mV	6.93×10^{-7}	94.08	198.45	75.98
10^{-3}M	-2 mV	4.45×10^{-7}	87.46	117.36	84.56

As it can be seen on Table 1, the anodic and cathodic slopes decrease with increasing concentration of SMX. The decrease of anodic slope is correlated to the inhibition of anodic oxidation of the metal while the decrease of cathodic slope is attributed to reduction of hydrogen evolution reaction. This suggests that the metal surface is covered by protective layer, probably an oxide inhibitor complex, which acts as a barrier to charge carriers [20, 21]. According to these results, SMX act as mixed type inhibition mode with predominantly anodic inhibition [22]. This behavior would indicate that the SMX behave as a mixed type inhibitor.

3.2. EIS Results

The Nyquist and Bode phase representations of the impedance behavior of the brass in the artificial acidic rainwater with and without the addition of various concentration of SMX are respectively shown in Figure 3 and Figure 4.

Increasing the concentration of SMX increases the diameter of the capacitive loop which indicates an increase in the charge transfer resistance of brass corrosion. The increase in resistance proved an increase in surface coverage. Bode plots of brass in inhibited artificial rainwater containing optimum concentration of SMX with different immersion time are shown in figures 5 and 6. The percentage inhibition efficiency (IE%) is calculated from the charge transfer resistance value using the following relation.

$$IE(\%) = \frac{R_{ct}-R_{ct}^{0}}{R_{ct}} \times 100 \qquad \text{[eq.3]}$$

where R_{ct} is the charge transfer resistance in presence of inhibitor and R_{ct}^{0} is the charge transfer resistance without inhibitor.

In the absence of SMX EIS spectrum displays two not clearly resolved time constants related to the capacitive loops. The high frequency (HF) capacitive loop is related charge transfer process, while the low frequency one concerns a diffusion process through a layer of corrosion products. It is found that R_{ct} values increased in presence of the inhibitor, whereas C_{dl} values found to be decreased. The decrease of C_{dl} is attributed to adsorption of SMX on the metal surface. From the Bode phase plot, a continuous increase of the phase angle shift with increasing concentration was clearly observed, obviously correlated to the increase of inhibitor adsorbed on the brass surface. The IE(%) calculated from impedance data shows is good agreement with the values obtained from polarization curves.

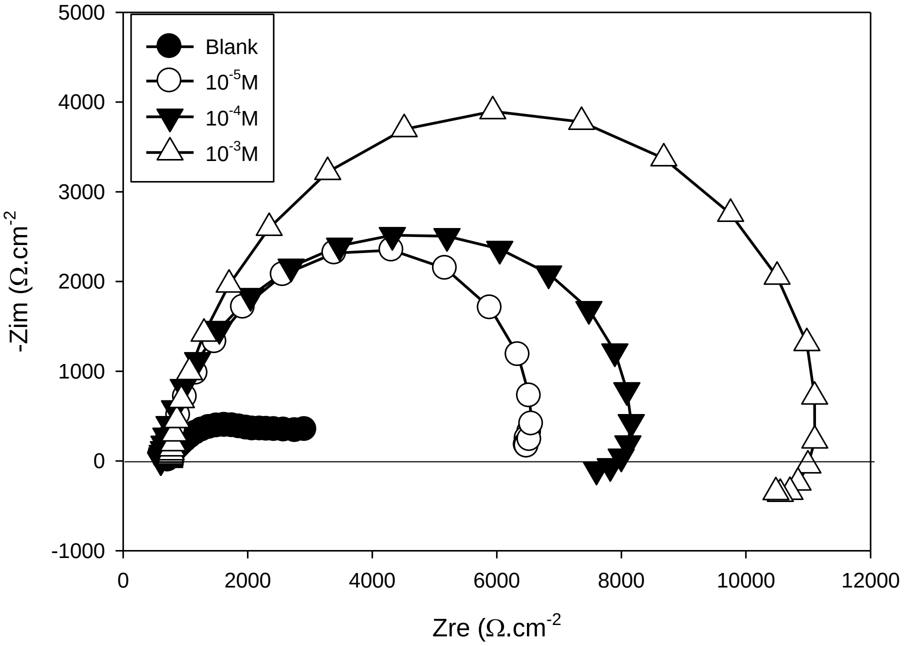

Figure 3. EIS diagram in Nyquist representation of brass in the electrolyte without and with various concentrations of SMX.

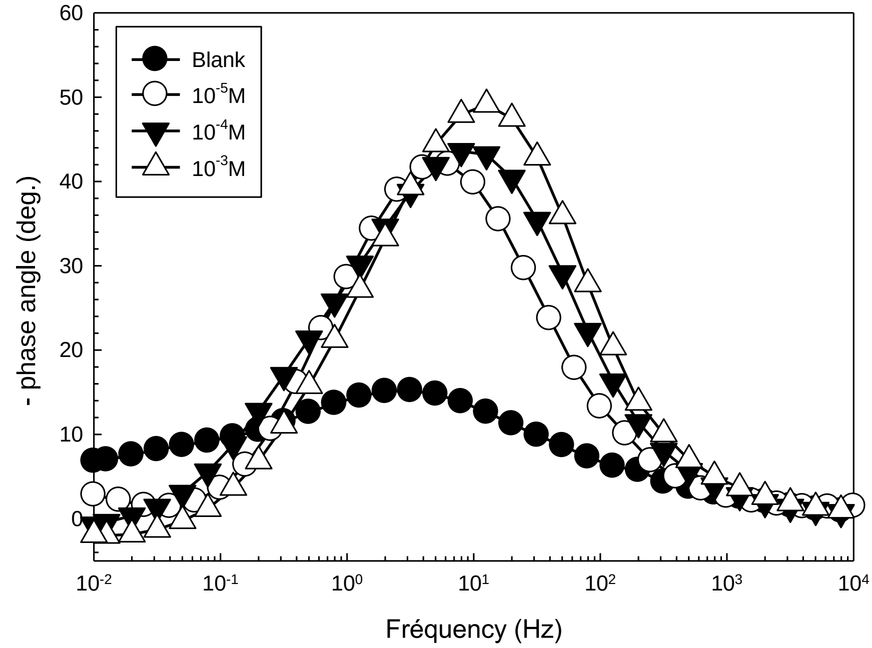

Figure 4. EIS diagram in Bode phase representation of brass in the electrolyte without and with various concentrations of SMX.

Table 2. EIS parameters for the corrosion of brass in the synthetic rainwater at different concentration of SMX

Concentration	*R_s (ohm)*	*Y_0(×10^6 nSs^n/ cm^{-2})*	*n*	*R_{ct}(ohm)*	*IE(%)*
Blank	711	255.9	0.76	1930	-
10^{-5}M	694	28.5	0.81	6253	69.13
10^{-4}M	692	26.5	0.83	7766	75.14
10^{-3}M	703	11.3	0.81	10560	81.72

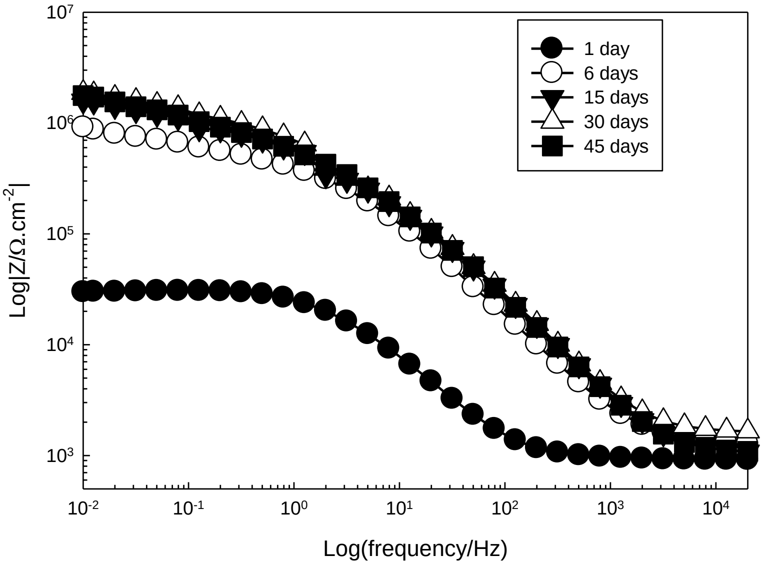

Figure 5. Evolution as function of time in artificial acidic rainwater with 10^{-3}M inhibitor concentration of the impedance in Bode modulus plots

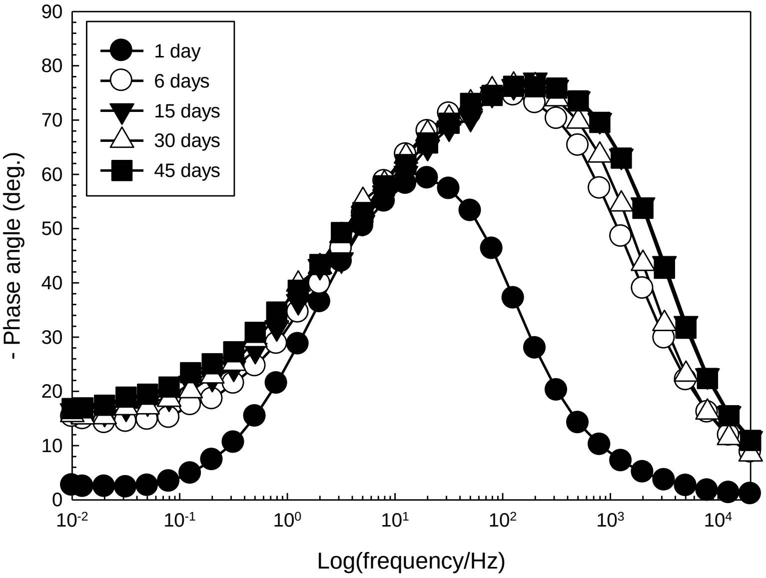

Figure 6. Evolution as function of time in artificial acidic rainwater with 10^{-3}M inhibitor concentration of the impedance in Bode phase plots

When EIS measurements were carried out in time, leaving the samples immersed in the solution, a continuous increase of impedance magnitude were observed. Due to the wide values of the impedance responses, the impedance spectra are presented in Bode plots. The total impedance, starting from about 3.1 $\times 10^4$ $\Omega.cm^{-2}$ after 1 day immersion time, reaches 1.8 $\times 10^6$ $\Omega.cm^{-2}$ after 15 days, indicating an important decrease of the corrosion attack. These results are in agreement with polarization curve, indicating a passivation behavior of the simples.

3.3. Surface analysis

Figures 7 show the optical micrograph of brass after immersion in the artificial acidic rainwater with and without SMX. The copper surface in Figure 7a appears to be attacked by the corrosive environment. In the presence of the inhibitor (10^{-3}M), we noted the formation of a deposit on the metal surface.

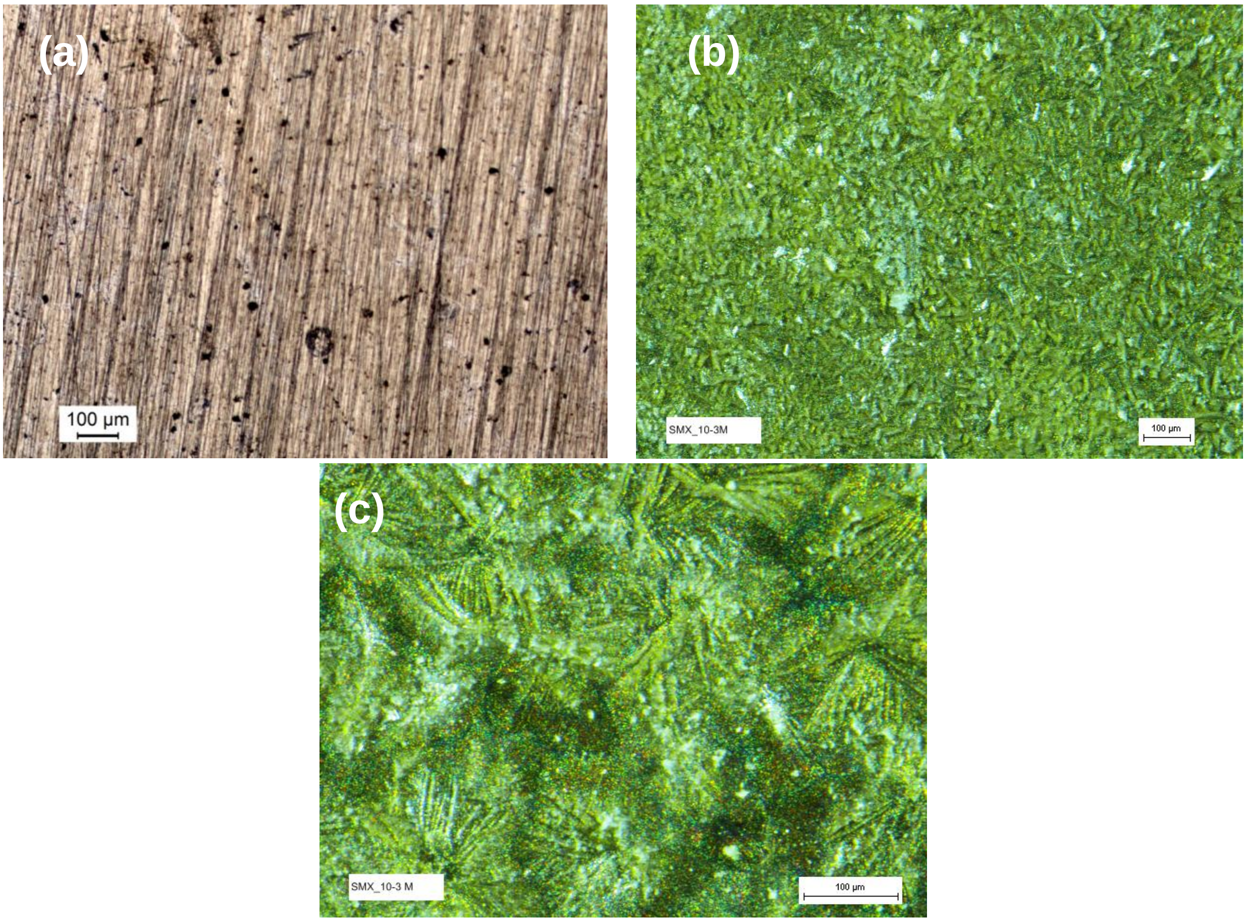

Figure 7. Optical micrographs of brass after immersion in the artificial acidic rainwater without and with 10^{-3} M of SMX. **(a)** after 24 hours in the blank solution; **(b)** after 24 hours in the solution SMX; **(c)** after 6 days in the solution of SMX

The aspect of the deposit changes during immersion. After 24 h immersion time (Figure 7b) the deposit appears roughed. When immersion time is about six days, the inhibited surface appears smoother and more compact. It is clear that a protective film developed and perfected over time onto to the brass sample when the corrosive solution contains SMX. Thus, the corrosion active sites present on sample surface were progressively blocked, leading to a decrease of the corrosion rate as polarization and EIS results indicated.

In order to understand the nature of the adsorbed film, SEM/EDX and FTIR analysis have been done on the surface after 2 days free immersion. SEM micrograph is given on Figure 8a. The EDX spectrum of the film (Figure 8b) shows the presence of C, N, O and S related to organic nature of the film, the copper and zinc signals are related to the brass substrate. It is obvious that this organic layer were made by SMX molecule adsorption.

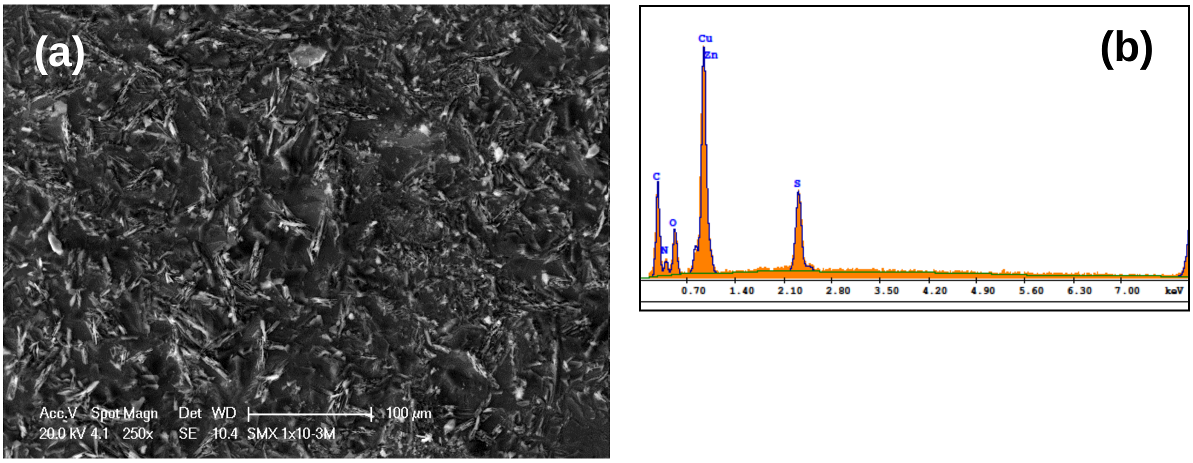

Figure 8. SEM and EDX analyses of brass immersed in the artificial rainwater (pH = 4) containing 10^{-3}M of SMX

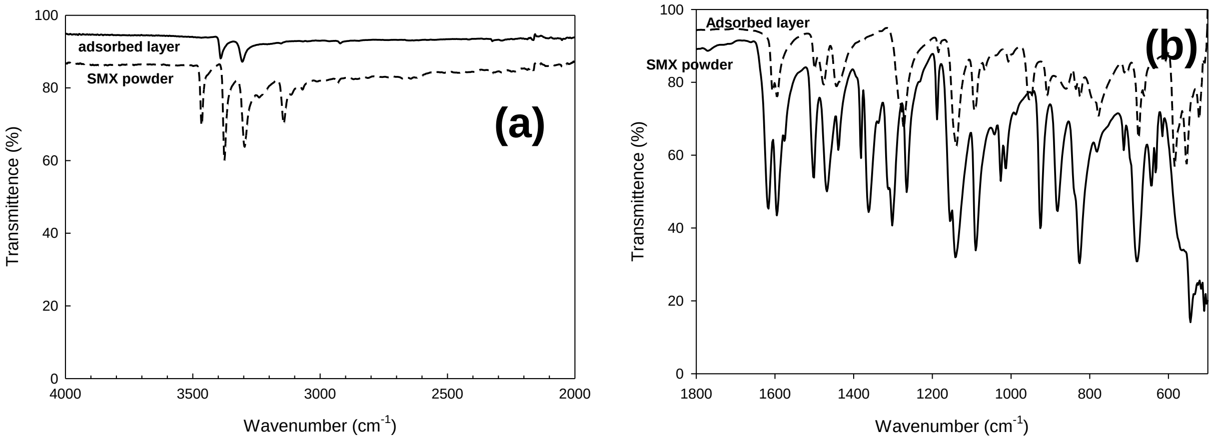

Figure 9. FTIR spectra of SMX powder and the adsorbed layer of immersed brass sample

In the FTIR spectrum of SMX (figures 9a and 9b) the bands observed at 3467 and 3374 cm^{-1} are assigned to antisymmetric and symmetric vibrations of aniline NH_2 group, respectively, in agreement with literature where Kanagarj and Rao [19] had observed these bands at 3467 and 3378 cm^{-1}, respectively. The band at 3298 cm^{-1} is assigned to the sulfonamide NH stretching vibration of SMX. In the adsorbed layer spectra, NH_3 antisymmetric and symmetric vibrations of the SMX shifted upon coordination toward a lower wave number compared with the free SMX molecule. These negative shifts could be due to an interaction between the aniline NH_2 groups and copper ions only, since Kanagaraj and Rao shown that in presence of zinc ions, the aniline NH_3 remain free [23]. It is also noticed the disappearance of the band at 3298 cm^{-1} (due to sulfonamide NH stretching of free ligand) in the adsorbed layer spectrum, indicating that the sulfonamide NH group was deprotonated during complex formation.

On figure 9b, it is observed that the most part of peaks are present indicating the correspondence of adsorbed layer with SMX, but a lack of absorption band is noticed at 1380 cm^{-1}. The disappearance of this peak is correlated to the involvement of isoxazole ring in the coordination of the ligand (possibly through nitrogen) to Cu atoms [23].

4. CONCLUSION

The inhibition effect of SMX on brass corrosion in artificial acidic rainwater can be summarized as follows:

- Potentiodynamic polarization results indicated the SMX is a mixed type inhibitor for the brass. When SMX concentration reached 10^{-4}M, both of cathodic and anodic corrosion are significantly inhibited and no significant change of the open circuit potential direction was observed. The inhibition efficiency increase with the increasing inhibitor concentration.
- EIS results also showed an increase of charge transfer resistance (R_{ct}) and decrease of double layer capacity. The continuous increase of R_{ct} value during 45 days immersion time test, observed with highest inhibitor concentration, is correlated to an improvement of inhibition efficiency over time.
- Optical microscopy, SEM/EDX and FTIR analysis of the brass surface after immersion in the synthetic rainwater containing the SMX revealed adsorption and good surface coverage of the inhibitor molecules.

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