Aromatic quinoxaline as corrosion inhibitor for bronze in aqueous chloride solution

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Abstract. A new corrosion inhibitor, viz. 3-ethyl-6-méthyl-quinoxalin-2-one, 1-benzyl-6-methyl-quinoxalin-2-one, 2-benzyloxy-3,6-dimethyl-quinoxaline, 1-benzyl-3-methyl-quinoxalin-2-one, were synthesized in the laboratory. Their influence on the inhibition on corrosion of bronze in aqueous chloride solution (3% NaCl) was studied by electrochemical polarization methods and weight-loss measurements. The impact of temperature on the effectiveness of the substances mentioned above has been determined between 20 and 60°C. The results showed that the corrosion resistance was greatly enhanced in the presence of inhibitor and that the effectiveness depends on some physicochemical properties of the molecule, related to its functional groups. These compounds act through the formation of a protective film on the surface of the alloy.

Keywords. Bronze; inhibitors; quinoxalin compounds; chloride solution; electrochemical studies.

1. Introduction

Heterocyclic organic compounds containing nitrogen, sulphur or oxygen atoms are often used to protect copper and copper alloy metals from corrosion. Among them, azoles compounds like triazoles, imidazoles and thiazoles have been intensively investigated as effective copper and copper alloys corrosion inhibitors (Patel *et al* 1977; Xue and Ding 1990; Kuznetzof 1996; El-Sayed *et al* 2007; Kosec *et al* 2007). Benzotriazole (BTA) is one of the most efficient inhibitor for copper and its alloys (Gerengi *et al* 2009; Khaled 2009). The BTA effectiveness has been related to the formation of Cu–BTA film (Tromans and Sun 1991) which is considered to be insoluble and polymeric (Xue and Ding 1990).

However, in line with environmental protection requirements, the use of BTA is nowadays quite limited, as toxic inhibitors that are widely used in industrial processes should be replaced with new environmental inhibitors. The use of non-toxic imidazoles derivatives, oximes and quinolines have very good inhibiting properties for Cu in NaCl media (Antropov *et al* 1978; Lisac *et al* 1998; Elmorsi and Hassanein 2003; Lee 2003).

Copper-based alloys (bronzes) containing alloying elements such as aluminum, nickel and iron offer a good combination of mechanical properties and corrosion resistance. Aluminum enhances the properties of castings, nickel improves corrosion resistance and iron increases tensile strength (Meigh 2000; Wharton *et al* 2005). Consequently, bronzes are widely used in a variety of marine applications such as pump casting, valves and heat exchanger.

The anodic dissolution of bronze shows many featured in common with the dissolution of copper, a simplified anodic reaction being the formation of the dichlorocuprous anion (Wharton *et al* 2005; Wang *et al* 2006)

$$Cu + 2Cl^- \rightarrow CuCl_2^- + e^-.$$
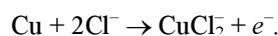
Similar mechanism was proposed for corrosion of copper in chloride media by many researchers (Lee and Nobe 1986; Barcia *et al* 1993). At chloride concentrations lower than 1 M, the mechanism of copper dissolution can be expressed as

$$Cu + Cl^- \rightarrow CuCl + e^-,$$

$$CuCl + Cl^- \rightarrow CuCl_2^-.$$
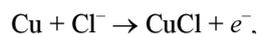
At chloride concentration > 1 M, higher cuprous complexes such as $CuCl_4^{3-}$ are formed (Crundwell 1992). In the apparent Tafel region, the anodic dissolution of copper and the diffusion of soluble $CuCl_2^-$ from outer Helmholtz plane into the bulk solution occur (Lee and Nobe 1986).

The cathodic reaction in neutral solution is

$$O_2 + 2H_2O + 4e' \rightarrow 4OH^-.$$
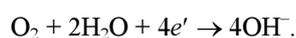
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The use of copper corrosion inhibitors in such conditions is necessary because no true passivation layer can be expected.

The aim of the present work was to investigate inhibiting properties of various quinoxalin derivatives in near neutral 3% sodium chloride solution on the corrosion of copper alloy (bronze).

2. Experimental

3-Ethyl-6-methyl quinoxalin-2-one (P4), 1-benzyl 3,6-dimethyl quinoxalin-2-one(YA1), 2-benzyloxy-dimethyl-3,6-quinoxalin1-benzyl (YA2), 1-methyl quinoxalin-2-one(YA3) tested as inhibitors were prepared (figure 1) in the following steps:

(I) A mixture of threonine (0·018 mol) and *o*-phenylenediamine (0·018 mol) in 40 mL of HCl 5,5N, was refluxed for 72 h, then cooled to room temperature and washed with a saturated solution of Na_2CO_3. The precipitate was filtered off and recrystallized from ethyl alcohol and gave pure product (yield 65%).

(II) Alkylation: To a solution prepared by dissolving 0·0057 mol of quinoxaline in 40 mL of DMF, was added 0·0069 moles of the alkylating reagent, potassium carbonate and tetra-*n*-butylammonium bromide.

The solution was stirred for 4 h at room temperature. The mixture was then filtered off, and the solvent was removed under reduced pressure. The residue was washed with dichloromethane. After performing a second filtration, and evaporating the solvent, pure products were obtained after recrystallization from ethyl alcohol.

Figure 1. Molecular structure of tested inhibitors.

All compounds prepared were characterized by their ^1H NMR and ^{13}C NMR spectra which were recorded on a Bruker AMWB 300 spectrometer:

*3-Ethyl-6-méthyl-quinoxalin-2-one (P4); m.p.: 140–142°C, ^1H RMN ($CDCl_3$)

δ: 0·7 ppm (*t*, 3H, CH_3); 1·5 ppm (*q*, 2H, CH_2); 2·45 ppm (*s*, 3H, CH_3), ^{13}C RMN ($CDCl_3$)

δ: 10·7, CH_3; 21·2, CH_3, 25·0, CH_2, 126·5; 138·8; 143·5 =CH; 129·9; 130·8; 137·1; 154·9; 155·4 Cq

*1-Benzyl-6-methyl-quinoxalin-2-one (YA1), m.p.: 96–98°C

RMN ^1H ($CDCl_3$)

δ: 2·41 (S, 3H, CH_3); 2·65 (S, 3H, CH_3); 5·49 (S, 1H, NCH_2); 7·05–7·71 (*m*, 8H, Har)

RMN ^{13}C ($CDCl_3$)

δ: 20·85 CH_3; 21·93 CH_3; 46·02 NCH_2
114·41; 114·66; 125·21; 127·07; 127·85; 129·11 Cq
133·70; 135·58; 140·45; 155·63; 157·39; 158·64 H arom.

*2-Benzyloxy-3,6-dimethyl-quinoxaline (YA2), m.p. = 120–122°C

RMN ^1H ($CDCl_3$)

δ: 2·55 (*S*, 1H, CH_3); 2·67(*S*, 1H, CH_3); 5·56 (*S*, 1H, OCH_2); 7·28–7·85 (*m*, 8H, Har)

RMN ^{13}C ($CDCl_3$)

δ: 20·67 CH_3; 21·69 CH_3; 68·14 OCH_2
126·32; 126·55; 127·55; 127·80; 128·74; 131·06 Cq
136·72; 136·97; 137·15; 140·02; 156·38; 193·52 64 H arom.

*1-benzyl-3-methyl-quinoxalin-2-one (YA3), m.p.: 86–88°C

RMN ^1H ($CDCl_3$)

δ: 2·60 (S, 3H, CH_3); 5·44 (S, 2H, NCH_2); 7·16–7·36 (*m*, 9H, Har)

RMN ^{13}C ($CDCl_3$)

δ: 21·70 CH_3; 45·91 NCH_2
114·44; 123·67; 126·87; 127·70; 128·93; 129·57; 129·59 H arom.
132·61; 132·93; 135·26; 155·30; 158·52 Cq.

Electrochemical measurements carried out in a conventional three electrodes set up were used, the reference being of saturated calomel. A working electrode was a copper alloy (bronze) disc protected by a thermoretractable sheath. It was connected to the axis of a rotating electric motor, the rotation speed (*w*) could be regulated from 0 to 4000 (tr/mn) and the standard speed used in this study was 1000 (tr/mn) unless otherwise specified.

Before starting each experiment, the electrode was abraded with grade 1000 silicon carbide emery paper, rinsed in water and dried with hot air. Polarization curves were performed by a EGG 263A potentiostat-galvanostat and controlled with EGG corrosion analysis software Model 352 SoftCorr with 500 $\mu V \cdot s^{-1}$ scan rate. Free corrosion time before polarization was 15 min. Optimum concentration was determined for each inhibitor at 25°C. Experiments at other temperatures were conducted with these concentrations only.
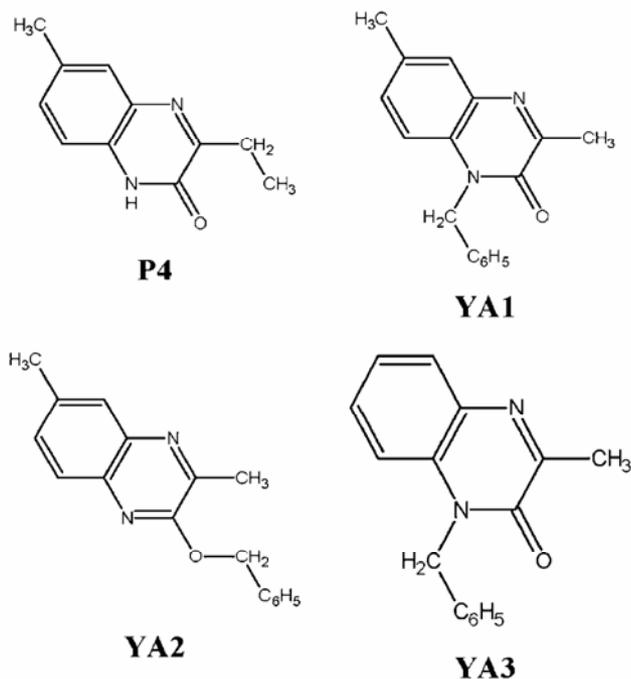
The electrode used in the electrochemical measurements had an area of 1·45 cm². The composition of the material studied is shown in table 1.

For the gravimetric measurements, the copper alloys were abraded with emery paper to a 1200 metallographic finish and rinsed in bidistilled water, after which they were air dried. The weight loss measurements were carried out after 8 days of immersion time. The aggressive solutions (3% NaCl) were prepared from analytical grade NaCl with bidistilled water. All tests have been performed at room temperature (20°C) in aerated solution.

3. Results and discussion

3.1 *Corrosion behaviour of bronze in 3% NaCl*

The cathodic curve of bronze electrode in aerated 3% NaCl is shown in figure 2. It was characterized by a current plateau corresponding to the oxygen diffusion reaction.

Nevertheless, there was a strong increase of this cathodic current with the rotation electrode (w). Figure 3 shows the variation of the limiting current density vs $w^{1/2}$ for different potentials. It is clear that at −1000 and −800 mV/s.c.e. the obtained variation is linear and presents an ordinate different from zero at the origin. This result shows the intervention of a process of mass transfer (diffusion). To determine whether the kinetics depends only on the diffusion or other processes, we draw the curves (I^{-1}, $w^{-1/2}$).

The representation of the same experimental data in reciprocal coordinates (I^{-1}, $w^{-1/2}$) gives also straight lines,

but it does not go through the origin of the axis, and we suggested interpretations developed by Bonnel *et al* (1983) and Deslouis *et al* (1993): mixed kinetics, i.e. electron transfer-mass transfer, for the cathodic reaction, or/and the existence of a porous layer in which mass transport only depends on molecular diffusion.

3.2 *Inhibitors with optimum concentration*

The cathodic potentiostatic curves of copper alloy in 3% NaCl with and without addition of organic compounds at 25°C are illustrated in figure 4. The maximum decrease in I_{cor} was at 5×10^{-3} M for each of the compounds. The electrochemical parameters obtained from these curves are given in table 2.
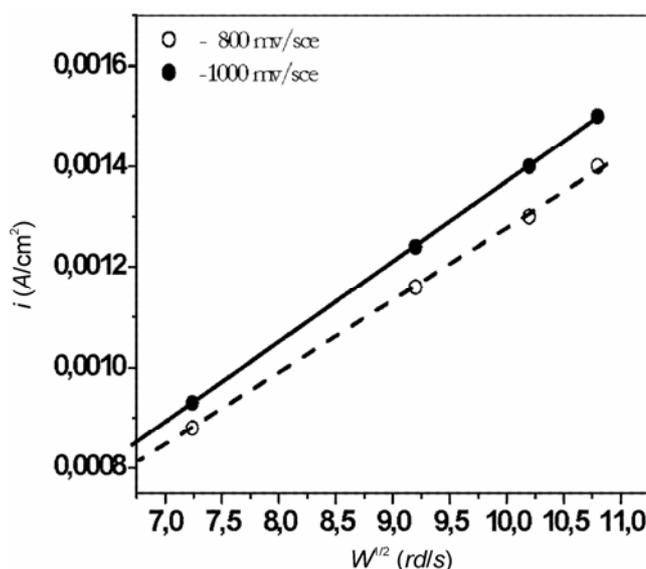
Figure 3. Variation of i according to $W^{1/2}$ for different cathodic potentials for copper alloy in 3% NaCl.

Table 1. Composition (% wt) of the alloy.

Element	Fe	Ni	Al	Cu
% in weight	4·2	8·97	8·66	78·26

Figure 2. Cathodic polarization curves of copper alloy in 3% NaCl solution at W = 1000 tr/mn.

Figure 4. Cathodic polarization curves of copper alloy in 3% NaCl without and with the addition of 5×10^{-3} M of P4, YA1, YA2 and YA3.

Table 2. Corrosion parameters for copper alloy in 3% NaCl with and without the addition of different concentrations of BTA obtained at 25°C, by Tafel extrapolation method and gravimetric measurements.
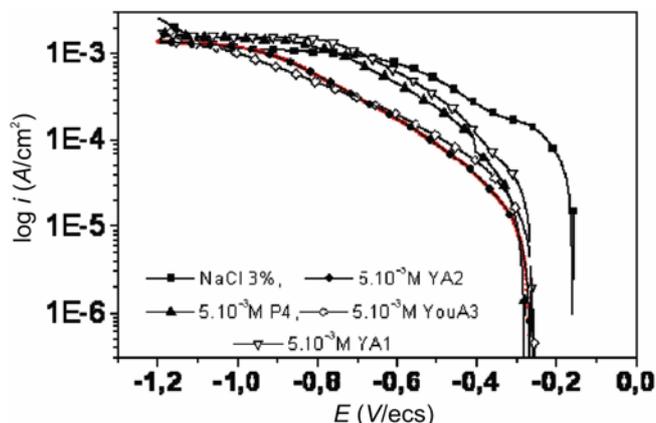
C (mol/l)	I_{corr} (A/cm^2)	E_{corr} (V/ECS)	E (%)	ΔP (mg·cm^{-2}·j^{-1})	E (%)
NaCl 3%	$3\cdot5 \times 10^{-4}$	$-0\cdot194$	–	$0\cdot35$	–
10^{-3} BTA	3×10^{-6}	$-0\cdot139$	99	$0\cdot0012$	$99\cdot7$
5×10^{-3} YA1	$1\cdot7 \times 10^{-5}$	$-0\cdot253$	$88\cdot6$	$0\cdot042$	88
5×10^{-3} YA3	$1\cdot8 \times 10^{-5}$	$-0\cdot282$	89	$0\cdot041$	88
5×10^{-3} P4	7×10^{-6}	$-0\cdot260$	95	$0\cdot022$	94
5×10^{-3} YA2	$6\cdot8 \times 10^{-6}$	$-0\cdot266$	96	$0\cdot009$	97
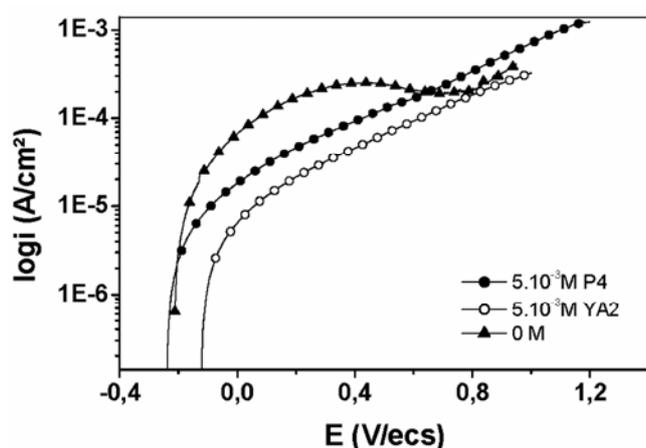
Figure 5. Anodic polarization curve of copper alloy in 3% NaCl without and with the addition of 5×10^{-3} M of P4 and YA2.

Table 3. Electrochemical parameters of copper alloy 3% NaCl added compounds at 5×10^{-3} M at different temperatures.

Temperature (°C)	Electrolyte	I_{cor} (A/cm^2)	E (%)
20	NaCl 3%	$3\cdot5 \times 10^{-4}$	–
	NaCl 3% + BTA	$2\cdot5 \times 10^{-6}$	$99\cdot3$
	NaCl 3% + YA2	$6\cdot7 \times 10^{-6}$	98
	NaCl 3% + P4	$8\cdot3 \times 10^{-6}$	$97\cdot6$
	NaCl 3% + YA3	$1\cdot95 \times 10^{-5}$	$94\cdot4$
	NaCl 3% + YA1	$2\cdot04 \times 10^{-5}$	94
30	NaCl 3%	$4\cdot9 \times 10^{-4}$	–
	NaCl 3% + BTA	$4\cdot96 \times 10^{-6}$	99
	NaCl 3% + YA2	$1\cdot2 \times 10^{-5}$	$97\cdot5$
	NaCl 3% + P4	$1\cdot64 \times 10^{-5}$	$96\cdot6$
	NaCl 3% + YA3	$2\cdot98 \times 10^{-5}$	94
	NaCl 3% + YA1	$3\cdot2 \times 10^{-5}$	93
40	NaCl 3%	5×10^{-4}	–
	NaCl 3% + BTA	$1\cdot74 \times 10^{-5}$	$96\cdot5$
	NaCl 3% + YA2	$2\cdot57 \times 10^{-5}$	95
	NaCl 3% + P4	$3\cdot14 \times 10^{-5}$	94
	NaCl 3% + YA3	$4\cdot2 \times 10^{-5}$	92
	NaCl 3% + YA1	$4\cdot77 \times 10^{-5}$	90
50	NaCl 3%	$6\cdot1 \times 10^{-4}$	–
	NaCl 3% + BTA	$6\cdot11 \times 10^{-6}$	98
	NaCl 3% + YA2	$5\cdot2 \times 10^{-5}$	91
	NaCl 3% + P4	$5\cdot8 \times 10^{-5}$	$90\cdot5$
	NaCl 3% + YA3	$7\cdot1 \times 10^{-5}$	88
	NaCl 3% + YA1	$7\cdot6 \times 10^{-5}$	$87\cdot5$
60	NaCl 3%	$7\cdot5 \times 10^{-4}$	–
	NaCl 3% + BTA	$8\cdot96 \times 10^{-5}$	83
	NaCl 3% + YA2	$1\cdot28 \times 10^{-4}$	86
	NaCl 3% + P4	10^{-4}	$85\cdot8$
	NaCl 3% + YA3	$1\cdot06 \times 10^{-4}$	$85\cdot7$
	NaCl 3% + YA1	$1\cdot13 \times 10^{-4}$	85

The addition of inhibitor induced an important decrease of the corrosion current. The inhibitor efficiency was found to be 97% for inhibitor YA2, 94% for inhibitor P4 and 88% for inhibitors YA1 and YA3. The inhibitor efficiency was calculated using the following relation

$$E\% = \left(1 - \frac{I'_{cor}}{I_{cor}}\right) \times 100,$$

where I_{cor} and I'_{cor} are the corrosion current densities in absence and in presence of the inhibitor, respectively.

As can be seen from figure 4, the inhibitors act by shifting the corrosion potential and decreasing the cathodic current densities. The lowest value of I_L was recorded for YA. According to table 2, all the inhibitors studied present an effectiveness beyond 80%. The inhibitors act also by decreasing the anodic current densities (figure 5).

To investigate the performance of the inhibitor, the electrode surface was examined by optical microscope, after corrosion test in 3% NaCl (figure 6). In the presence of P4 and YA2, the state of the surface improves distinctly (figure 6b) and did not present any corrosion form, indicating the inhibiting effect of these compounds.

The inhibitor efficiency ($E\%$) was also calculated from mass loss measurements using the relation

$$E\% = \left(1 - \frac{W}{W_0}\right) \times 100,$$

where W and W_0 are rate of corrosion (g cm^{-2} h^{-1}) with and without inhibitor, respectively. The data obtained are given in table 3, for an immersion period of 48 h.

This comparative study (table 3) shows that $E\%$ values obtained by both methods, electrochemical and gravimetric, are in good agreement and confirm also that P4 and A2 are excellent inhibitors.

Figure 6. Optical micrographs of copper alloy specimens before and after an anodic scan until + 500 mV/s.c.e. in: NaCl 3% (**a**), NaCl 3% + 5 × 10⁻³ M BTA (**b**), NaCl 3% + 5 × 10⁻³ M P4 (**c**).

Table 4. Activation energies for copper alloy in 3% NaCl without and with the addition of investigated inhibitors.

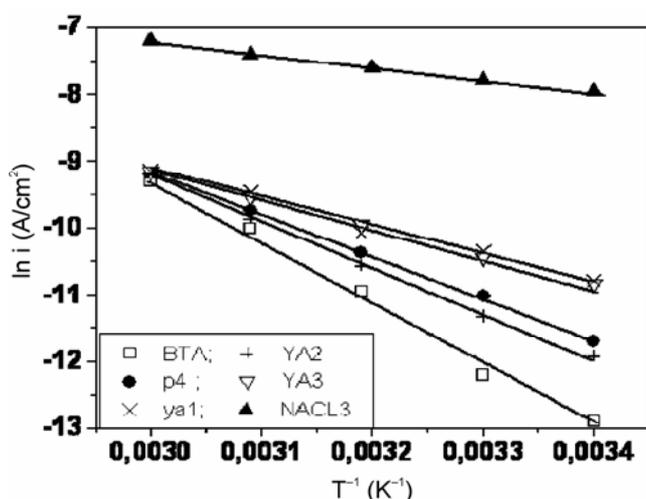| Solution	E_a (kJ/mol)
3% NaCl	16·64
BTA	80·74
YA2	56·58
P4	55·3
YA1	35·8
YA3	31·6

Figure 7. Arrhenius straight lines calculated from corrosion rate of copper alloy in 3% NaCl, 3% NaCl + 5 × 10⁻³M BTA, NaCl 3% + 5 × 10⁻³ M P4, NaCl 3% + 5 × 10⁻³ M YA2.

3.3 *Effect of temperature*

The corrosion rates of copper alloy in 3%NaCl in the absence and the presence of various inhibitors at 20, 30, 40, 50 and 60°C are listed in table 4. For each inhibitor, the corrosion rate of bronze increased with temperature.

The inhibition efficiency of the compounds is less affected by increasing the temperature, for which *E*% becomes less than 85% when tested at high temperature (60°C).

It has been suggested by many authors (Arslan *et al* 2009; Khaled 2009) that the most organic inhibitors act by adsorption on the metal surface. The adsorption of inhibitors takes place through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, multiple bonds or aromatic rings.

Comparison of the inhibition efficiencies obtained

YA2 > P4 > YA3 > YA1,

reveals that we assist really to an intramolecular synergistic. By referring to compound P4, the alkylation of N with the formation of amide functional group reduces the efficiency of inhibitory molecules, in the case of the compounds YA1 and YA3. However, the alkylation O with the formation of ester functional group improves the effectiveness of inhibitory molecules, in the case of compounds YA2. This change in structure, in particular functional group, affect strongly electronic density of donor atom and hence the quality of the bond metal/ inhibitor.

It has been suggested that the adsorption of organic inhibitors mainly depends on some physicochemical properties of the molecule, related to its functional groups, to the possible steric effects and electronic density of donor atom (Machnikova *et al* 2008; Roque *et al* 2008; Varvara *et al* 2008; Arslan *et al* 2009).

The corrosion reaction can be regarded as an Arrhenius type process, the rate of which is given by

$$i_{corr} = A\exp(-E_a/RT),$$

where E_a is activation corrosion energy, R the universal gas constant and A a constant.

Arrhenius plots for corrosion rate of copper alloy are given in figure 7; values of different activation energies calculated are shown in table 5. It was clear that activation energies increased in the presence of inhibitor. The increase in the activation energy may be attributed to chemisorptions of inhibitors at the alloy surface and the corrosion process proceeds through a different mechanism in the presence of the inhibitor (Antropov *et al* 1978; Sankarapavinasam *et al* 1992).

The chemisorptions should be explained on the possible interaction of *p*-orbitals of the inhibitor with *d*-orbitals of the surface atoms, which induces greater adsorption of the inhibitor molecules onto the surface of bronze, leading to the formation of a corrosion protecting film. Nevertheless, this protective film must be studied using techniques for surface analysis (FT–IR, ESCA) in order to investigate this layer.

The increase in activation energy is particularly pronounced in case of YA2 and P4 indicating the strong adsorption of these inhibitors on the surface of the material. These inhibitors showed the best efficiency.

4. Conclusions

(I) Electrochemical study and weight loss measurements showed that all of the quinoxalines compounds (P4, YA1, YA2 and YA3) acted as efficient corrosion inhibitors of bronze in 3% NaCl solution.

(II) The maximum inhibition efficiency reached for many of them exceeded 90%.

(III) The observed protecting effect of these inhibitors was affected by the nature of the functional group: maximum inhibitor efficiency of about 97% was obtained for 2-benzyloxy-dimethyl3,6-quinoxalin1-benzyl (compound with ester functional group).

(IV) The inhibition efficiency did not change significantly with increase in temperature, and the addition of quinoxalines led to an increase of activation corrosion energy.

(V) The inhibitors tested act by chemical adsorption leading to the formation of inhibitory films. Nevertheless, this protective film must be studied using techniques for surface analysis.

Acknowledgement

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