“BABES - BOLYAI“ University, Cluj-Napoca

Faculty of Chemistry and Chemical Engineering

AXINTE ROXANA NADINA (BOSTAN)

PhD DISSERTATION

SUMMARY

NEW NON-TOXIC CORROSION INHIBITORS FOR PROTECTION OF BRONZE EXPOSED TO ENVIRONMENTAL FACTORS

Jury:

President:

Prof. Ionel Cătălin POPESCU, Babeș-Bolyai University, Cluj-Napoca

Scientific Advisor:

Prof. Liana - Maria MURESAN

Members:

Prof. Nicolae VASZILCSIN, Politehnica University of Timisoara

Conf. Simona VARVARA, 1 Decembrie 1918 University, Alba Iulia

Conf. Graziella TURDEAN, Babeș-Bolyai University, Cluj-Napoca

Defense: 25th of September 2015

TABLE OF CONTENTS

II. ORIGINAL CONTRIBUTIONS

Keywords: bronze, corrosion, inhibitors, thiadiazoles derivates, phenothiazine derivatives, adsorption, quantum chemical calculation, artificial patina, impedance spectroscopy.

INTRODUCTION

As a result of interaction with the environment (water, soil, and atmosphere), in the process of corrosion, on the surface layer of bronze corrosion products occur, called "patina".

The continued growth of environmental pollution leaves its mark on bronze objects exposed to the atmosphere. Acid rain caused by air pollutants (CO, CO_2, SO_X, NO_X) are the main cause of corrosion that appears on the surface of heritage bronze objects exposed to outdoor conditions and thus the necessity to protect them by using different methods.

The use of corrosion inhibitors, on their own or in a mixture with various lacquers, waxes or synthetic resins, is a common practice for the protection of bronzes. The most effective corrosion inhibitors for copper and its alloys have proven to be organic substances that contain in their molecule heteroatoms with high electron density (O, N, S) which are able to easily make coordinative bonds with the metal surface, but many of the these substances are toxic and non-biodegradable.

Among the corrosion inhibitors used so far, benzotriazole (BTA) is known from 1947 as a very effective corrosion inhibitor for copper and its alloys [1] in wide ranges of temperature and pH. Recent studies show that stabilization of bronze artefacts with BTA is not always successful; the treatment can alter the appearance of patina layer, by darkening areas containing cuprite, malachite and nantokite. Apart from these, the most serious shortcoming of BTA's is its toxicity and the fact that is not biodegradable. In what regards the inhibitory action of these compounds, research, including those done by electrochemical methods, showed that it is due to physical or chemical adsorption of the inhibitor on the metal surface.

Finding new bronze corrosion inhibitors, efficient, unharmful to humans and the environment are current interests for both specialists in conservation/restoration and for physicists, chemists (electrochemists), etc. who find a challenge in both deciphering the mechanisms of the formation of corrosion products in contact with the environment (air, water, soil) and also in their way of interacting with inhibitors.

In the context of current concerns, the overall objective of this thesis is the identification and evaluation with the help of electrochemical methods of new non-toxic corrosion inhibitors and of effective protective coatings from the category of lacquers and resins for the corrosion protection of uncovered and covered with artificial patina bronze exposed to the atmosphere and in particular to acid rain.

In order to achieve the overall objective the following specific objectives were achieved:

- The determination of the inhibitory efficiency of the organic compounds from the class of thiadiazole and phenothiazine derivatives in the corrosion process of bronze, at different pH values in an aqueous medium in order to simulate acid rain.
- The investigation of the corrosion behaviour of bronze covered by patina in the absence and in the presence of inhibitors.
- The study of the electrochemical behaviour of the artificial patina, independent of the metal surface and in the presence of thiadiazole derivatives, using carbon paste electrodes.
- The study of the protective effect on bronze of two types of layers (an acrylic resin and a nitrocellulose lacquer in which are incorporated inhibitors) useful in the practice of the restoration-conservation of objects made of bronze.

This paper has two parts, a literature study and a research part containing my own personal contributions.

In the first part a study on the research literature was done regarding the influence of environmental factors (water, air, soil) on the process of bronze corrosion, corrosion products formed from the interaction with the environment protection methods used and electrochemical methods of investigation used in deciphering the mechanisms of formation of corrosion products and the evaluation of the protective properties exhibited by various classes of inhibitors.

The second part, that of my own contributions, includes experimental results obtained from the use of electrochemical methods (polarization curves, electrochemical impedance spectroscopy, cyclic voltammetry) and non-electrochemical (SEM, EDX, Langmuir adsorption isotherms, quantum calculations) in three research directions: (i) assessing the protection effect of four thiadiazoles derivatives for artificially patinated bronze and for bare bronze in acidic (pH 3) medium; (ii) the evaluation of the protective effect on the bronze in an acidic medium of pH 5 shown by 4 phenothiazine derivatives at various concentrations, and (iii) assessing the ability to protect bronze in an acidic medium of pH 5 of two types of coatings (Paraloid B72 acrylic resin and nitrocellulose lacquer) mixed at concentrations determined to be optimal of the studied inhibitors.

II. ORIGINAL CONTRIBIUTIONS

INTRODUCTION

The overall objective of this thesis is the identification and evaluation with the help of electrochemical methods of new non-toxic corrosion inhibitors and of effective protective coatings from the category of lacquers and resins for the corrosion protection of uncovered and covered with artificial patina bronze exposed to the atmosphere and in particular to acid rain.

In order to achieve the overall objective the following specific objectives were achieved:

- The determination of the inhibitory efficiency of the organic compounds from the class of thiadiazole and phenothiazine derivatives in the corrosion process of bronze, at different pH values in an aqueous medium in order to simulate acid rain.
- The investigation of the corrosion behaviour of bronze covered by patina in the absence and in the presence of inhibitors.
- The study of the electrochemical behaviour of the artificial patina, independent of the metal surface and in the presence of thiadiazole derivatives, using carbon paste electrodes.
- The study of the protective effect on bronze of two types of layers (an acrylic resin and a nitrocellulose lacquer in which are incorporated inhibitors) useful in the practice of the restoration-conservation of objects made of bronze.

3. EXPERIMENTAL CONDITIONS

3.1. Reagents and materials

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.

The electrolyte solutions (0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$) were prepared using analytical grade reagents by Merck.

Benzotriazole, 2-mercapto-5-amino-1,3,4-thiadiazole and 2-mercapto-5-methyl-1,3,4-thiadiazole used were produced by Sigma Aldrich, UK.

The phenothiazine derivatives, 2-mercapto-5-acetylamino-1,3,4-thiadiazole and 2-mercapto-5-phenylamino-1,3,4-thiadiazole used in this research were synthesized in the laboratory.

The bronze sample was transferred into the electrochemical cell and the measurements were carried out in an aqueous solution of 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$, acidified to pH 3 and 5 by addition of dilute H_2SO_4.

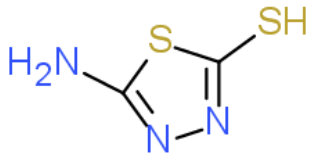
3.2. Electrochemical cell

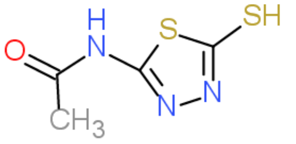
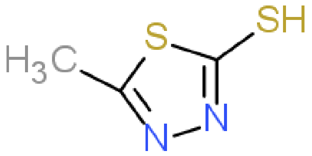
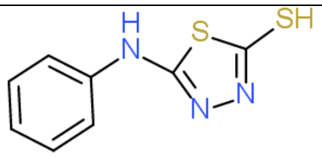
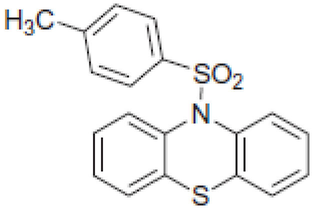
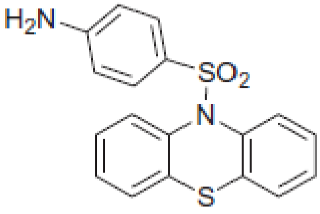
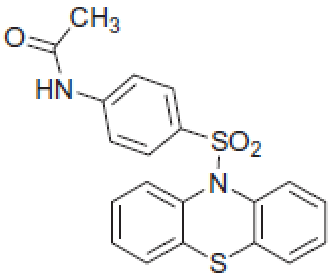
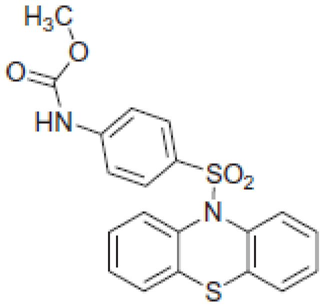
A three-electrode cell was used for the electrochemical experiments. The counter-electrode was a large platinum grid and an Ag/AgCl, KCl_{sat} or a saturated calomel electrode (SCE) was used as reference electrode.

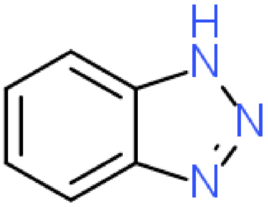
3.4. Inhibitors

Four innoxious thiadiazoles derivates and four phenothiazine derivatives (Table 5) have been investigated as bronze corrosion inhibitors in a solution containing Na_2SO_4 and $NaHCO_3$ that simulates acid rain in an urban environment, at different pH value. For comparison reasons, the inhibiting effect of benzotriazole (BTA) was also examined.

Table 5. The names and chemical structures of the organic inhibitors under study

INHIBITOR	STRUCTURE	ABBREVIATION
THIADIAZOLES DERIVATES		
2-mercapto-5-amino-1,3,4-thiadiazole		MAT

INHIBITOR	STRUCTURE	ABBREVIATION
2-mercapto-5-acetylamino-1,3,4-thiadiazole		MAcAT
2-mercapto-5-methyl-1,3,4-thiadiazole		MMeT
2-mercapto-5-phenylamino-1,3,4-thiadiazole		MPhAT
PHENOTHIAZINE DERIVATIVES		
10-(toluene-4-sulfonyl)-10*H*-phenothiazine		**TSP**
10-(4-amino-benzenesulfonyl)-10H-phenothiazine		**AmSP**
10-(4-acetanido-benzenesulfonyl)-10H-phenothiazine		**AcaSP**
10-(4-methyilcarbamate-benzenesulfonyl)-10*H*-phenothiazine		**MecSP**
BENZOTRIAZOLE		

INHIBITOR	STRUCTURE	ABBREVIATION
		**BTA**

3.5 Protective coatings

For artificially bronze patinate protection was investigate two types of coatings : an acrylic resin (Paraloid B72) and an nitrocellulose lacquer.

RESULTS AND DISCUSSIONS

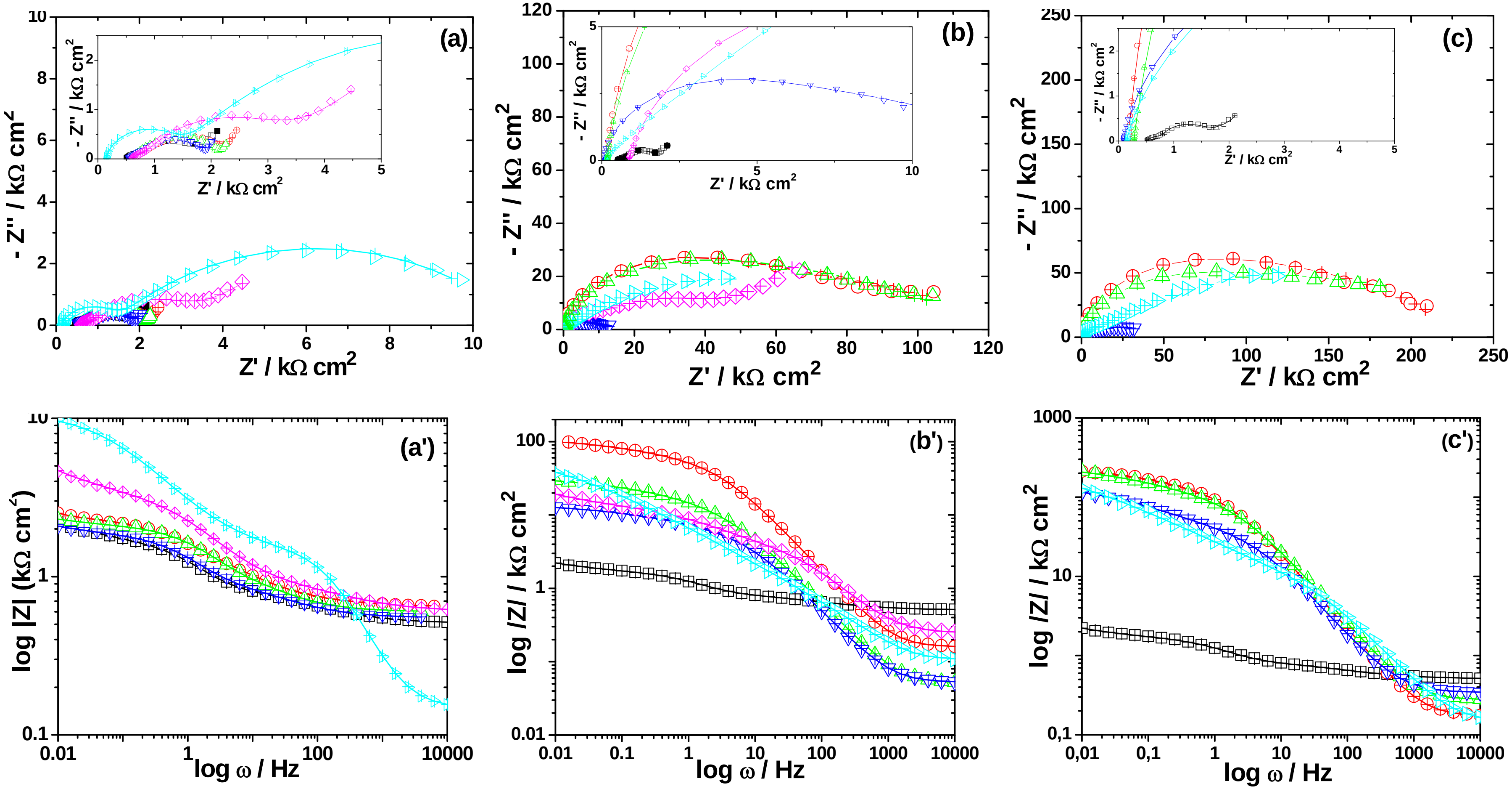
4. INHIBITOR EFFECT OF THIADIAZOLE DERIVATIVES FOR NAKED BRONZE AND ARTIFICIALLY PATINATED BRONZE IN ACIDIC MEDIA(pH=3)

4.1. Inhibitor effect of thiadiazole derivatives for naked bronze in acidic media(pH=3)

4.1.3. Electrochemical impedance spectroscopy (EIS)

The protective effectiveness of the investigated thiadiazole derivatives on the bronze corrosion was evaluated by impedance spectroscopy measurements. The experiments were performed after 1 hour of immersion in the corrosive solution (pH 3) to ensure the stability of the system during the impedance measurement [84].

The impedance spectra for naked bronze immersed in acidic carbonate/sulphate solution (pH 3) in the absence and in the presence of different concentrations of organic inhibitors (0.1; 1 și 5 mM), represented as Nyquist and Bode plots in Figure 18.


(a)
- Z'' / kΩ cm²
Z' / kΩ cm²
(b)
- Z'' / kΩ cm²
Z' / kΩ cm²
(c)
- Z'' / kΩ cm²
Z' / kΩ cm²
(a')
log |Z| (kΩ cm²)
log ω / Hz
(b')
log /Z/ / kΩ cm²
log ω / Hz
(c')
log /Z/ / kΩ cm²
log ω / Hz

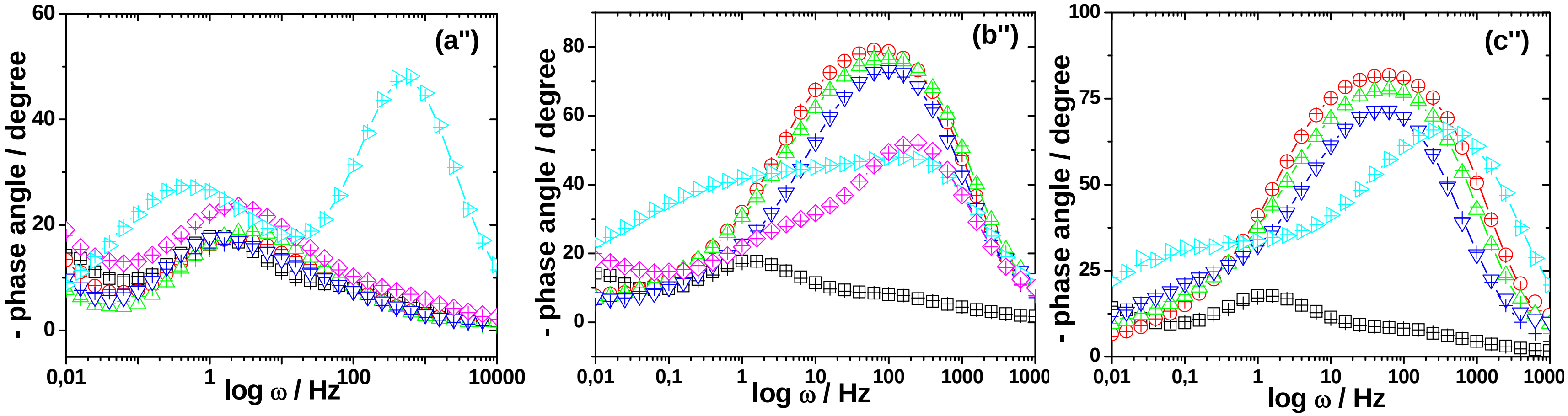
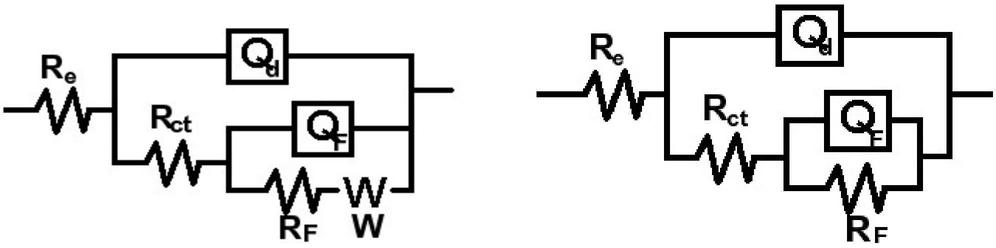


Figure 18. *Nyquist and Bode plots for the corrosion of naked bronze in acidic carbonate/sulphate solution (pH 3) in the absence (□) and in the presence of organic inhibitors (○) MMeT; (Δ) MAT; (∇) MAcAT; (◊) MPhAT; (▷) BTA, at various concentrations (mM): 0,1 (a-a'-a"), 1 (b-b'-b") şi* **5** *(c-c'-c"). Symbols corresponds to the experimental data and the line with cross (—+—) to the calculated data*

The impedance data corresponding to the naked bronze corrosion in pH 3 electrolyte without and with the addition of the lowest concentration of thiadiazole derivatives were analyzed in terms of the electrical equivalent circuit presented in Figure 19a.



(a) (b)

Figure 19. *Equivalent electrical circuits used to reproduce the experimental data*

In this model, 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. The parameters R_F - Q_F are related to an oxidation - reduction process involving a reaction intermediate (*i.e.* Cu^+ ions) [98, 119], while W stands for the Warburg impedance.

The impedance spectra corresponding to bronze corrosion in the presence of high concentrations of organic compounds were accurately fitted to a (2RQ) electrical equivalent circuit presented in Figure 18b. The origins of the two R-Q couples were ascribed to the contributions mentioned above. A (2RC) ladder circuit was formerly used by K. Marusic et al. [119] to explain bronze corrosion in the presence of 4-methyl-1-p-tolylimidazole.

In the equivalent circuits from Figure 19, instead of capacitance elements, we have used constant phase elements (CPEs) represented by the terms, Q and n. The use of CPEs as substitutes for pure capacitive elements is widely applied nowadays to account for the deviations induced by the surface roughness and various other non-homogeneities of the metallic surface [168], resulting from the presence of the impurities, inhibitor adsorption, formation of porous layer, insufficient polishing etc.

The variations of the calculated R and C parameters as a function of the thiadiazole derivatives concentration are illustrated graphically in Figure 20. For comparison reasons, the fitting parameters obtained when benzotriazole (BTA) was used as bronze corrosion inhibitor in acidic solution (pH 3) were also included in Figure 20.

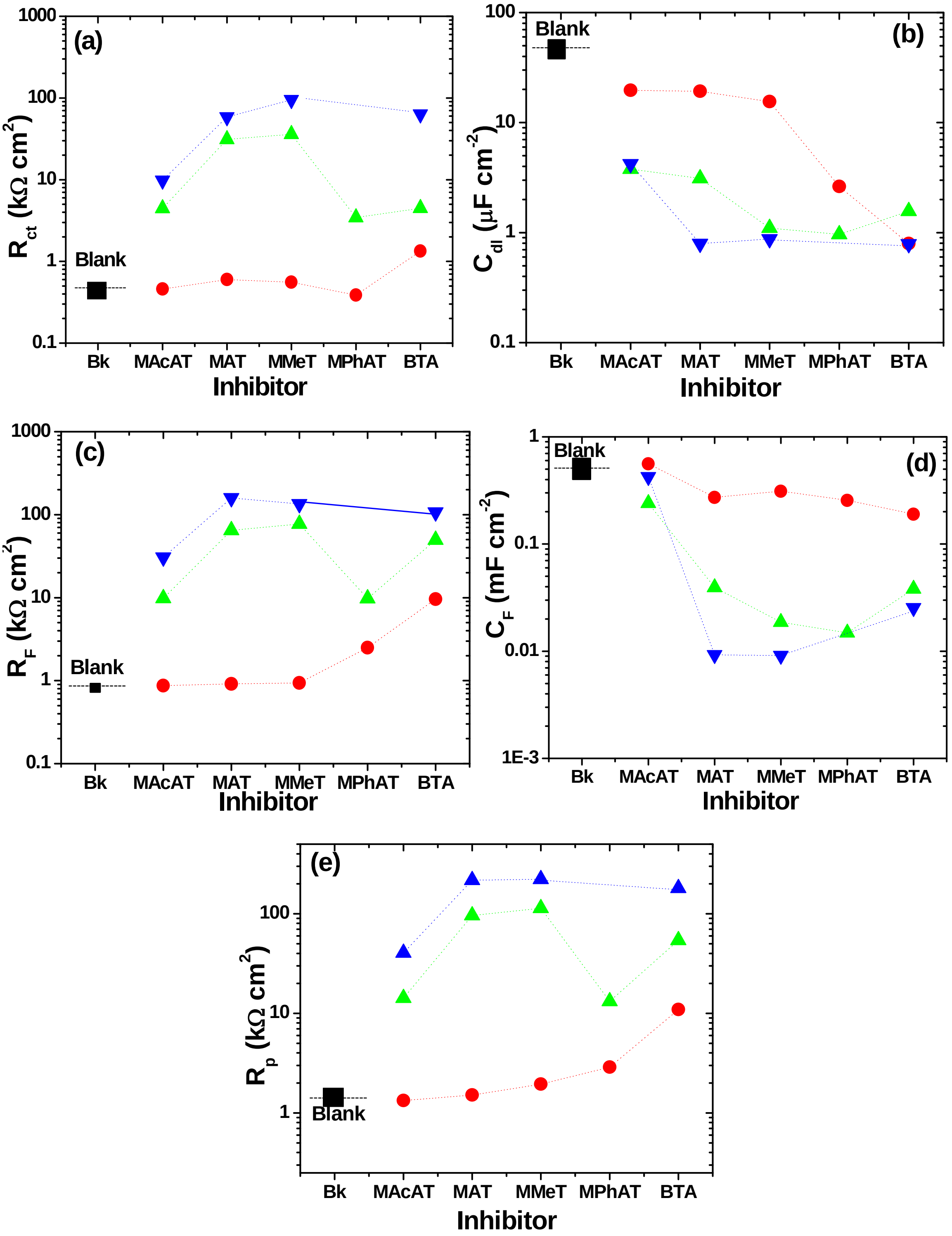


Figure 20. *Evolution of the R-C parameters calculated from for naked bronze in acidic carbonate/sulphate solution (pH 3), as a function of the organic inhibitors concentration (mM): (■) 0; (●) 0.1; (▲) 1; (▼) 5*

The best protective effect was observed in the presence of MMeT. The R_{ct} value was almost 250 times higher when 5 mM MMeT was added into the corrosive solution compared to its absence.

The variation of the polarisation resistance values, R_p, calculated as the sum of the resistances, R_{ct} and R_F is shown in Figure 20(e) as a function of the organic inhibitors concentration.

The R_p values were used to calculate the inhibition efficiency, (IE), as a function of the thiadiazole derivatives concentration (Table 7), according to equations (3) and (4).

As it is shown in Figure 20, the inhibitive effect of the investigated thiadiazole derivatives is scarce at their lowest concentrations (0.1 mM). This can be explained as there is a partial diffusion control of the dissolution process, which means that at low concentrations of organic compounds the inhibition degree might be limited not only by the partial coverage of the electrode surface with adsorbed thiadiazole derivatives, but also by the oxygen diffusion process [170]. The substantial increases of the inhibition efficiency values observed at high concentrations of inhibitors (≥ 1mM) could be due to the formation of a highly protective layer of the organic compounds on the bronze surface that prevents the diffusion process and significantly decrease the bronze corrosion rate.

In the investigated experimental conditions, at their optimal concentrations (5mM), MMeT and MAT show a more protective effectiveness on bronze corrosion compared to BTA (Table 7).

Table 7. *Influence of the corrosive solution pH and of the organic inhibitors concentration on the inhibition efficiency values*

Inhibitor conc. (mM)	***IE (%)***								
	MMeT		**MAT**		**MAcAT**		**MPhAT**		**BTA**
	pH								
	3	**5**	**3**	**5**	**3**	**5**	**3**	**5**	**3**
0,1	38,9	86,5	21,6	-13,8	10,8	- 7,8	58,8	97,0	89,1
1	98,9	91,1	98,8	88,5	91,7	95,7	90,9	42,2	96,9
5	**99,5**	**92,6**	**99,4**	**95,9**	**97**	**-**	**-**	**-**	**99,1**

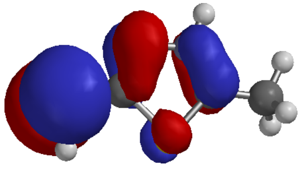
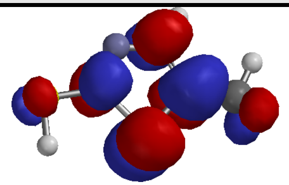
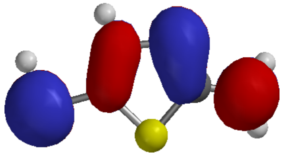
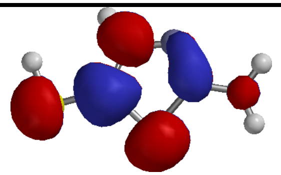
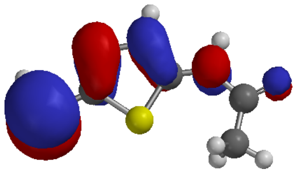
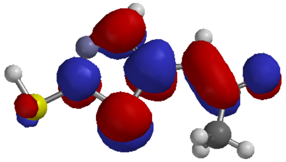
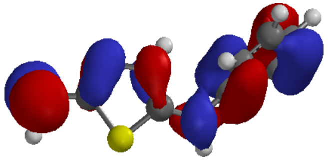
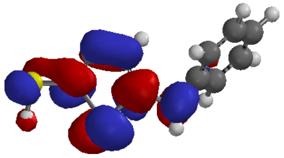
4.1.4 Quantum chemical calculations

In order to find a possible correlation between the experimental inhibition efficiencies and the electronic structures of the thiadiazole inhibitors, the minimum energy geometry of each derivative has been obtained starting with molecular mechanics optimization of the conformers generated within the Confanal module of Spartan'06 [61], followed by semi-empirical (PM3), HartreFock and 6-31G(d) B3LYP DFT [162-164]. The generated lowest energy conformers were further used in order to calculate the quantum molecular parameters, such as E_{HOMO}, E_{LUMO} and the ΔE energy gap, which are given in Table 8.

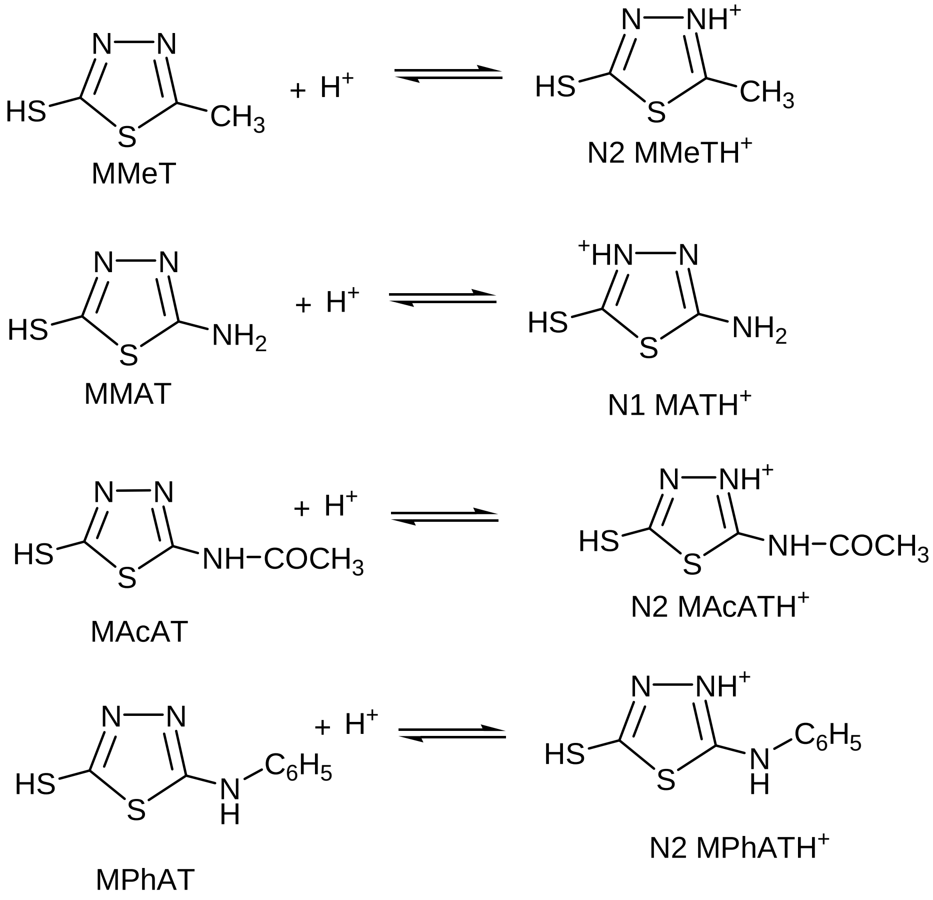
Modifications of the corrosion inhibition efficiencies of thiadiazole derivatives at pH 3 are most probably due to structural changes in the thiadiazole moiety following the protonation at one of the nitrogen atoms in the heterocycle. The protonation equilibria of the thiadiazole derivatives which may occur in acidic media (pH 3) are presented in Scheme 2.

According to E values in Table 9 the protonation of the N2-nitrogen atom in the thiadiazole ring appears to be favored in all cases, exception for MAT-derivative, probably due to the electron donor effect of the amino ($-NH_2$) substituent in position 5 of the heterocycle which orients the protonation towards N1. In the case of benzotriazole, the protonation takes place at N3 atom and the calculated value of ΔE is -4.775 eV.

Table 9. *Theoretical quantum chemical parameters of the protonated thadiazole derivatives and typical HOMO and LUMO densities distribution*

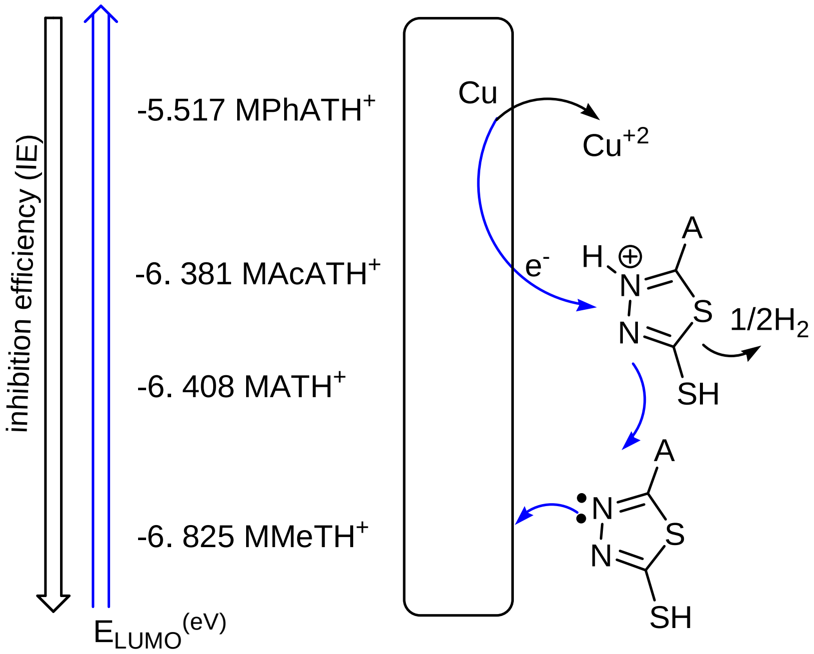
Compound	Protonated position	E (au)	E_{HOMO} (eV)	HOMO densities distribution	E_{LUMO} (eV)	LUMO densities distribution	ΔE (eV)
MMeT H^+	**N2**	**-1023**	**-11,528**		**-6,825**		**4,703**
MAT H^+	**N1**	-1039	-11,173		-6,408		4,765
MAcAT H^+	**N2**	-1192	-11,197		-6,381		4,816
MPhAT H^+	**N2**	-1270	-10,561		-5,517		5,044

The theoretical results obtained by B3LYP, 6-31G(d) method (Table 9) show that ΔE for the protonated species of thiadiazole derivatives and BTAH$^+$ lay in the following order: MMeT H$^+$ > MATH$^+$> BTAH$^+$> MAcAT H$^+$> MPhAT H$^+$ pointing in the same direction as the inhibition efficiency values obtained from EIS technique.



Scheme 2. *Protonation equilibrium of the thiadiazole derivatives in acidic media (pH 3)*

A possible mechanism of inhibition performed by the thiadiazole protonated species existing at pH 3 is suggested in Scheme 3 and involves in the first step a cathodic reduction on the bronze surface generating the neutral thiadiazole ring which further coordinates the cooper on the surface. The facility of the reduction processes may be directly correlated with the LUMO orbital energy, a lower energy value suggesting the easiness in accommodating the incoming electrons.



Scheme 3. *The possible mechanism of inhibition performed by the thiadiazole protonated species*

4.3. Partial conclusions

Completing our previously reported results referring to thiadiazole derivatives as efficient inhibitors of bronze corrosion in weakly acidic solution (pH 5) [121], the results obtained in the present paper showed that the anticorrosive performances of these inhibitors are affected by the pH of corrosive solution, since these compounds appears to be protonated in stronger acidic medium. In an attempt to better understand the influence of solution pH on the adsorption of the thiadiazole derivatives and to correlate their structural and electronic characteristics with the experimental inhibition efficiencies, the thiadiazole derivatives structures were investigated by Density Functional Theory (DFT) using hybrid B3LYP, 6-31G* model. A possible inhibition mechanism of the thiadiazole protonated species on bronze corrosion was proposed.

In the investigated experimental conditions, MMeT was proved to be the most promising corrosion inhibitor to be applied both on naked and artificially patinated bronze. Moreover, MMeT and MAT allow the stabilization of the patina layer leading to the protection of the bronze substrate and their effectiveness significantly increases with the immersion time in acidic corrosive solution (pH 3). Contrarily, BTA progressively looses its protection ability over time.

6. EVALUATION OF SOME PHENOTHIAZINE DERIVATIVES AS CORROSION INHIBITORS FOR BRONZE IN ACIDIC SOLUTIONS (pH 5)

6.2. Potentiodynamic polarization measurements

Figure 35 shows representative Tafel polarisation curves for bronze immersed in 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$ (pH=5) solution at 25^0C in the absence and presence of different concentrations of phenothiazine derivatives.

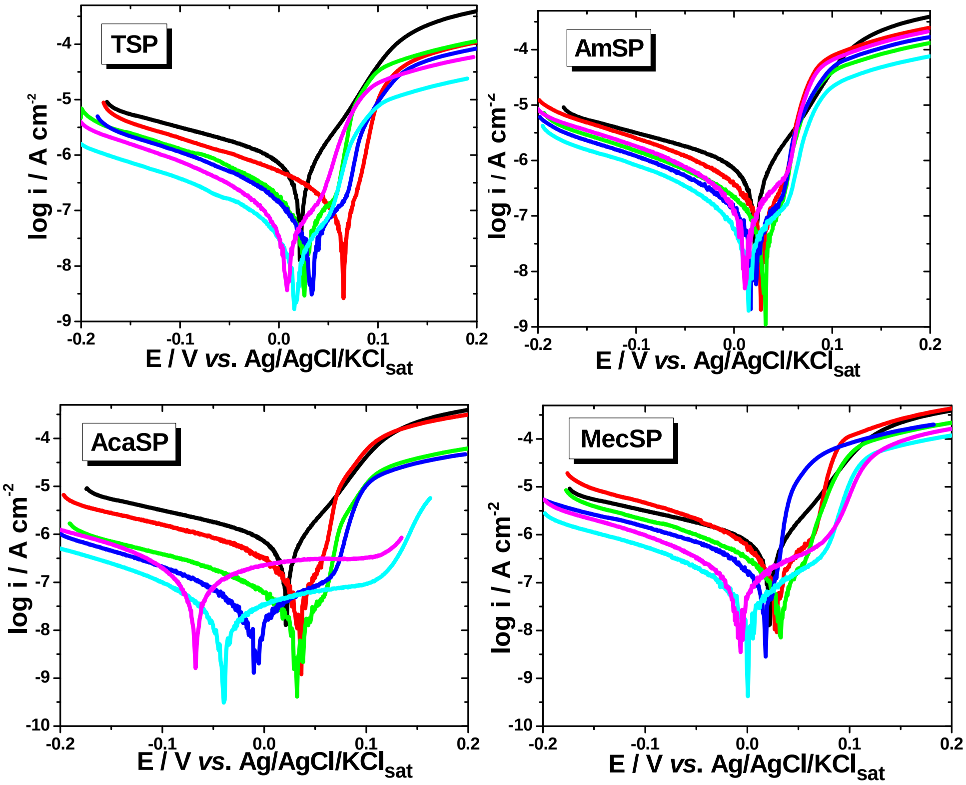


Figure 35. *Anodic and cathodic polarization curves (Tafel curves) for bronze in $Na_2SO_4/NaHCO_3$ (pH 5) solution without (—) and with various concentrations of phenothiazine derivatives (μM): (—)10,(—)25,(—)50,(—)75,(—)100.*

Electrochemical kinetic parameters, such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c and β_a) and corrosion current density (i_{corr}) were estimated by extrapolation of the Tafel lines and are presented in Table 12. The inhibition efficiencies (IE%) of the phenothiazine derivatives calculated according to equation (2) are also given in Table 12.

From Figure 35, it is clear that both the anodic metal dissolution and oxygen reduction reactions are hindered when phenothiazine compounds are added to the corrosive solution.

The values of the corrosion density significantly decrease with increasing phenothiazine derivatives concentrations up to 75 μM; then the i_{corr} values start to slightly increase at higher concentration of inhibitors (Table 12).

Table 12. *Corrosion parameters obtained from the polarization curves of the studied phenothiazine derivatives*

Inhibitor	**Conc. (μM)**	E_{corr} **(mV/Ag/AgCl)**	i_{corr} **(μA/cm^2)**	$-\beta_c$ **(mV/dec)**	β_a **(mV/dec)**	***IE* (%)**
Blank	0	22,44	0,659	172,85	46,39	-
TSP	10	66,25	0,189	49,04	15,53	71,32
	25	27,39	0,138	118,35	100,20	79,06
	50	32,52	0,085	77,41	75,55	87,10
	75	***17,023***	***0,057***	***77,44***	***66,85***	***91,4***
	100	-7,46	0,067	84,62	72,06	89,83
AmSP	10	22,83	0,243	129,89	79,27	63,13
	25	31,25	0,181	108,97	166,98	72,53
	50	17,40	0,148	140,91	169,16	77,54
	75	***14,19***	***0,121***	***97,767***	***91,506***	***81,8***
	100	5,23	0,174	85,80	99,03	73,60
AcaSP	10	38,37	0,139	45,388	18,818	78,91
	25	34,34	0,089	125,85	167,33	86,49
	50	-7,77	0,070	128,47	489,10	89,38
	75	***-39,96***	***0,058***	***128,47***	***489,10***	***91,2***
	100	-63,95	0,093	92,59	128,27	85,89
MecSP	10	28,08	0,260	69,82	66,09	60,55
	25	32,32	0,161	80,89	35,06	75,57
	50	17,68	0,108	49,03	11,16	83,61
	75	***1,20***	***0,068***	***108,29***	***118,11***	***89,7***
	100	-7,45	0,220	131,20	187,42	66,62

The decreasing of the current density values also reflects different protective behaviour of phenothiazine derivatives on bronze corrosion, as shown in the following sequence: AcaSP ≈ TSP > MecSP > AmSP.

In all cases, the inhibition degree of the studied compounds depends on their concentrations and molecular structures. Thus, the increase of the inhibitor concentration from 10 μM to 75 μM was accompanied by an increase of the IE values, *i.e.* from 78.9% to 91.2% for the most efficient compound, AcaSP. These results suggest that the phenothiazine derivatives act as fairly efficient adsorptive inhibitors on bronze corrosion, *i.e*. they reduce the anodic dissolution and also retard the oxygen evolution reaction, *via* blocking the active reaction sites of the metallic surface and, therefore, protect it from the corrosive effect of the electrolyte. However, it should be mentioned that an increase of phenothiazine derivatives concentrations to 100 μM leads to a decrease of the IE values.

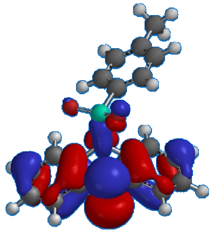
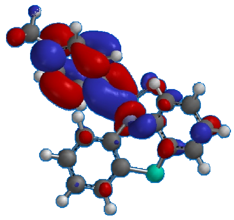
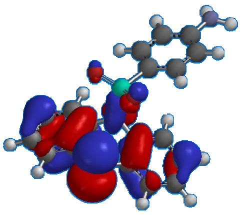
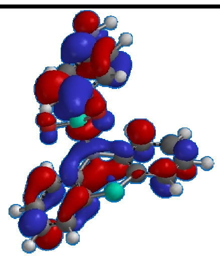
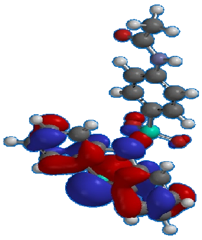
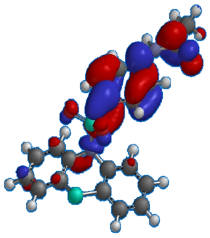
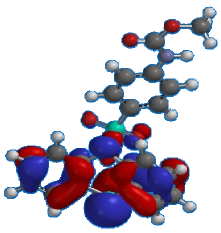
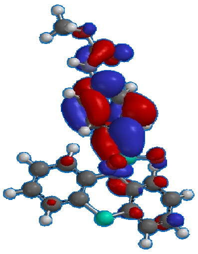
The changes of the anodic (β_a) and cathodic (β_c) Tafel slopes observed on the addition of phenothiazine derivatives indicate that the kinetics of anodic and cathodic processes are affected by the presence of the inhibitors in the corrosive media. Since no definite trend was observed in the shift of (β_a) and (β_c) values in the presence of different inhibitors, it was assumed that the investigated compounds act mainly as mixed-type inhibitors for bronze corrosion in solution containing Na_2SO_4 and $NaHCO_3$ at pH = 5.

Nevertheless, the shifts of E_{corr} values towards positive direction in the presence of low concentrations (10 -25 μM) of phenothiazine derivatives could be probably explained by a small domination of the anodic dissolution reaction. At higher concentrations of inhibitors (50 -100 μM), the corrosion potentials shift towards more negative values as compared to the E_{corr} value calculated for blank solution and a predominant control of the cathodic reduction reaction could be assumed.

6.4. Quantum chemical calculations

In order to find a possible correlation between the experimental inhibition efficiencies and the electronic structure of the phenothiazine inhibitors, the minimum energy geometry of each derivative has been estimated starting with molecular mechanics optimization of the conformers generated within the Confanal module of Spartan'06, followed by semi-empirical (PM3) and 6-31G(d) B3LYP DFT, followed by semi-empirical (PM3) and 6-31G(d) B3LYP DFT [161-164]. The generated lowest energy conformers were further used in order to calculate the quantum molecular parameters such as E_{HOMO}, E_{LUMO} and the HOMO-LUMO energy gap, which are given in Table 14.

Table 14. *Calculated quantum chemical parameters of the studied phenothiazine derivatives and the repartition of HOMO and LUMO densities*

Compus	HOMO	LUMO	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (Debye)
TSP			-5,65	-1,15	4,5	5,37
AmSP			-5,57	-0,86	4,7	7,18
AcaSP			-5,67	-1,26	4,4	3,07
MecSP			-5,72	-1,17	4,5	6,51

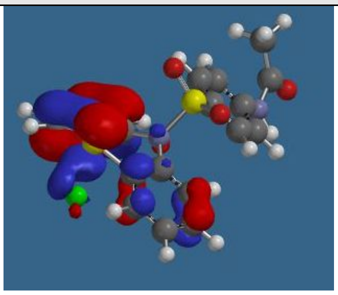
The theoretical data obtained by B3LYP, 6-31G(d) level of theory (Table 5) show that the absolute values of the energy band gap (ΔE) for phenothiazine derivatives lay in the following order: AcaSP < TSP < MecSP < AmSP, which is consistent with the calculated values of the inhibition efficiencies obtained from both, polarization curves and EIS techniques.

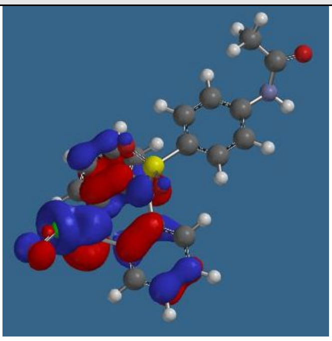
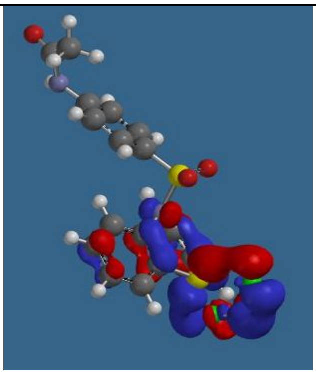
In the bronze alloy, the predominant metal is copper, a *d* type transition metal containing unoccupied atomic orbitals, characterized by a pronounced tendency to form coordination complexes with donor molecules. We suppose that the inhibition process is based on the formation of an insoluble and highly adherent donor-acceptor (DA) complex between the inhibitor and the copper and copper (I or II) oxide. The formation of these DA complexes imply the electron donation from the occupied π-molecular orbitals of the ligand into the vacant copper centered orbitals, possibly accompanied by retrodonor bonds formed by the donation from the metal to the vacant π-orbitals of the ligand.

An examination of the frontier molecular orbitals which could be involved in the bonding between the inhibitor and the copper, shows that at HOMO participate all the atoms in the phenothiazine core of the inhibitor, while LUMO is preponderantly distributed on the substituent, with one exception which occurs in the case of AmSP with a LUMO shared by the whole molecule, which shows the poorest inhibitor activity.

In order to better understand the inhibition of copper dissolution process by phenothiazine derivatives chemisorption on the bronze surface, molecular mechanics and semi-empirical (PM3) optimization were performed using model complexes such as Cu-, CuO- and Cu_2O - phenothiazine derivatives respectively. The well known electron donor properties of the phenothiazine core may lead to electronic interactions between the sulfur atom of the donor heterocyclic and the acceptor Cu or Cu oxides, as shown for example in the Table 15, where one can see the distribution of HOMO orbital between the sulphur atom from phenothiazine moiety and copper nucleus.

Table 15. *Theoretical quantum chemical parameters of the studied Cu-phenothiazine complexes and the repartition of HOMO densities*

Aca-Cu complex	**Repartition of HOMO densities on Cu-inhibitor complex molecule**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE (eV)**
AcaSP-Cu		-11,68	-4,62	7,06

Aca-Cu complex	**Repartition of HOMO densities on Cu-inhibitor complex molecule**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE (eV)**
AcaSP-CuO		-9,43	-1,48	7,95
AcaSP-Cu_2O		-8,13	-1,42	6,71

6.7. Partial conclusions

All investigated phenothiazine derivatives are fairly efficient inhibitors towards bronze corrosion in slightly acidic solution containing Na_2SO_4 and $NaHCO_3$ at pH=5, even in µM concentration range. Their inhibition efficiency increases with increasing the inhibitor concentrations up to the optimum value (75µM) and, at any given conditions, it decreases according to the following order: AcaSP > TSP > MecSP > AmSP.

The protection afforded by phenothiazine derivatives is due to their adsorption on the bronze surface forming a blocking barrier to corrosion process. The EDX analysis of the bronze surface exposed to inhibitor-containing solution confirmed the presence of nitrogen atoms on the electrode surface. The adsorption of these molecules on bronze in the corrosive solution obeys the Langmuir isotherm and the adsorption mechanism is typical of chemisorption.

The stability of the Cu-phenothiazine derivative complex depends essentially on the difference between interacted orbital energies. The absolute values of the standard free energy of adsorption and the dipole moments are in good agreement with the order of inhibition efficiency values calculated from the polarization curves and EIS techniques. A correlation between the energy gap of the phenothiazine derivatives molecules and their inhibition efficiencies was also put on evidence.

7. PROTECTIVE COATINGS FOR ARTIFICIALY PATINATED BRONZE

7.1. Corrosion protection of nitrocellulose laquer mixed with organic inhibitors

7.1.2. Monitoring the protective effect in time through electrochemical impedance measurements

The protective efficacy shown by the bare nitrocellulose lacquer or mixed with organic inhibitors (MMeT, MAT, AcaSP and BTA) was evaluated by electrochemical impedance measurements made over three months by intermittent immersion of the electrode in a solution of carbonate / sulphate (pH 5) which simulates urban acid rain.

Whatever the nature of the coating along the whole period of immersion in the electrolyte, the capacitive behaviour was observed over the entire domain of frequencies investigated.

Except bare nitrocellulose lacquer coverage, in the impedance diagrams of the coatings containing organic inhibitors, only one capacitive loop is visible, the impedance values are high and those of phase shift remain close to -90˚ on a fairly large frequency domain. As the exposure to corrosive environment grows, however, there is an emergence of a second loop of impedance diagrams and while there is a decline in the values of impedance and of phase shift. These observations suggest the emergence of a process of degradation of the nitrocellulose coatings, more pronounced after prolonged immersion in electrolyte and suggests that the electrolyte penetrates through the coating layer and reaches the metal surface [66].

To get more information on how organic inhibitors present in the nitrocellulose lacquer coating composition influence the effectiveness of coating in time we continued our research with simulations of impedance diagrams. To this end 2RQ circuit shown in Figure 48 was used. We need to mention that given the insignificant effectiveness of protective coating with AcaSP by comparison to bare nitrocellulose lacquer, its corresponding data were not further interpreted.

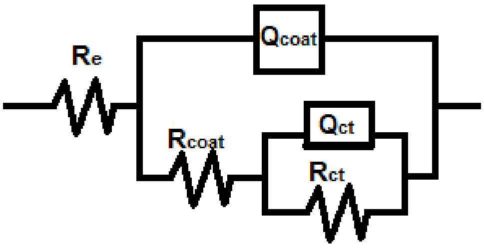


Figure 48. *Equivalent electrical circuits used to reproduce the experimental data*

We also state that the same circuit 2RQ was used by other authors to simulate impedance data corresponding to bronze electrodes chemicaly and electrochemicaly patinated and covered with Paraloid B-44 in which the inhibitors (4-methyl-1- (p-tolyl) imidazole and benzotriazole) were incorporated[187].

In the circuit in Figure 48, R_e is the electrolyte resistance, R_{coat} is the resistance of cover to the transfer of electrons and Q_{coat} is the constant phase element associated to the differential electrical capacitance of the coating; R_{ct} is the charge transfer resistance and Q_{dl} is a constant phase element characterizing the electrical double-layer capacitances at the bronze/electrolyte interface. The values of each of the elements from the equivalent electric circuit were calculated using the software ZSimpWin 3.21.

The analysis of R_{ct} and C_{dl} parameter values indicates that the highest charge transfer resistance is obtained in the case of MAT coating which once again confirms the significant anti-corrosive effect compared to the other coatings. It needs to be mentioned that the anticorrosion properties of MAT coating were very stable over time during the monitoring period. As expected, the electric double layer capacitance values are significantly reduced by comparison to the other coatings, fact which is illustrated in the Figure 50.

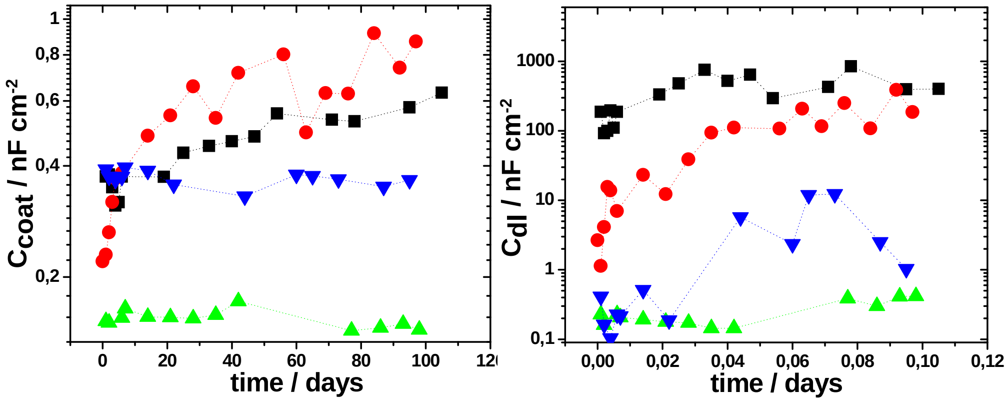


Figure 50. Time-changes of the capacitances from impedance data of the ertifially patinated bronze samples covered with nitrocellulose laquer withouth (■) and mixed with organic inhibitors (●)LacMMeT, (▲) LacMAT, (▼)LacBTA, at different immersion times in

$Na_2SO_4/NaHCO_3$ sollution at pH 5

For all the other coatings investigated, there is a decrease of R_{ct} values in time. At the start of the monitoring period, the corrosion rates are similar for BTA and MMeT coatings and higher than the corresponding R_{ct} values of bare nitrocellulose lacquer. In time, there is a significant decrease in the R_{ct} values, fact explained if we consider that the electrolyte penetrates through the pores of the coating, disseminates and comes into contact with the bronze surface and thus initiating a process of corrosion.

7.3. Partial conclusions

In conclusion, besides the thickness of the coating, the protective efficacy of these layers is determined by the nature of the used inhibitors. The significant protective effect on the patinated bronze showed by the nitrocellulose lacquer with MAT, proved to be the most effective coating (but also with the greatest thickness) of the ones investigated could be explained mainly by the physical barrier effect shown by this on the bronze patina, and also through the better inhibitory effect of MAT. It is possible that in the experimental conditions investigated, the high impermeability of this type of coating makes unlikely electrolyte penetration through pores which gives significant corrosion protection.

Conversely, in the case of bare nitrocellulose lacquer coatings and those with added MMeT and BTA, the data obtained showed that they have corrosion efficiency only for short exposure times (21 days). The penetration of electrolyte through the pores of the coatings leads to a decrease in their protective effect at longer exposure periods.

GENERAL CONCLUSIONS

1. The effect of corrosion protection on bronze of 4 thiadiazole derivatives and of 4 new phenothiazine derivatives, as well as two types of coatings (Paraloid B72 acrylic resin and a nitrocellulose lacquer) in experimental conditions simulating acid rain was assessed.

2. In the experimental conditions investigated, the results show that the effectiveness of inhibition in the protection of bare bronze and patinated bronze of the studied organic

compounds depends on their concentration in the corrosive medium, the time of contact of the surface with the solution containing the inhibitor as well as the electronic properties of those.

In the case of thiadiazole derivatives:

3. In the corrosive solution of carbonate / sulphate at pH 3 the results obtained by electrochemical impedance spectroscopy and polarization curves show that the anti-corrosion properties of the thiadiazole derivatives are reduced to very small concentrations of inhibitor, the maximum level of inhibition efficiencies are at a concentration of 5 mM for MMeT, MAT and 1 mM in MPhAT.

4. From the point of view of the mechanism of action, the results of the investigated thiadiazole derivatives as inhibitors for the protection of bronze in an acidic medium at pH 3, compared with those reported in literature for these compounds in an acid medium of pH 5, indicate that the action of it depends on the pH of the medium; in a strongly acidic medium they act under a protonated form.

5. The cyclic voltammograms recorded in the absence and in the presence of thiadiazole derivatives have shown that the inhibitory effect is predominantly manifested on the dissolution process of the reactive species in artificial patina, which was confirmed by the significant decrease of the power density, which the more pronounced was, the higher the concentration of MAT and MMeT was. These results are confirmed by electrochemical impedance spectroscopy measurements that highlight the stronger inhibitory effect of thiadiazole derivatives at high concentration levels compared with the one shown by BTA; the evolution in time of polarization resistance values vary in the following order: MMeT> MAT> BTA.

6. Under the experimental conditions investigated, MMeT present at a concentration of 5 mM in corrosive medium proved to be the most effective inhibitor, both for the protection of bare bronze and artificially patinated bronze.

In the case of phenothiazine derivatives:

7. All of the 4 new derivatives of phenothiazine investigated have been found to be effective corrosion inhibitors for bronze in the electrolyte that simulates acid rain of pH 5. The order of the values of inhibition efficiencies calculated by several methods for these compounds is: AcaSP> TSP> MecSP> AmSP. Their effectiveness increases with the increase of their concentration levels in corrosive environment, reaching the highest value for the concentration of 75µM. Surface analyzes conducted after the metal surface came in contact with the solution containing the inhibitor, at a concentration at which the inhibition efficiency

is maximal, confirmed the presence of the adsorbed inhibitor due to the presence of the nitrogen atom in the EDX spectrum.

8. The adsorption inhibitors follow Langmuir isotherm model, and the mechanism by which it is accomplished is by chemical absorption. The phenomenon of inhibition exerted by the phenothiazine derivatives is based on the formation of a donor-acceptor (DA) which is insoluble and very adhesive between the inhibitor and copper that is, oxides of copper (I or II). The stability of these complexes depends mainly on the energy difference of the frontier orbitals. Based on quantum calculations we determined that the calculated standard energy values were in the same sequence as the inhibition efficiencies values calculated on the basis of polarization curves and impedance spectra.

In the case of protective coatings:

9. From the results of the assessment obtained from the evaluation of protective properties of the two types of coatings studied, we can say that besides thickness, the protective efficacy of the layers is determined by the nature and the inhibitors used. Thus, under the experimental conditions investigated, the best protection for the patinated bronze is provided by the presence of MAT coating in the protection layer (be it the nitrocellulose lacquer or the Paraloid B72) which is clear from both the high values of $|Z|_{0.01Hz}$ and the longest period of maintaining these values constant.

10. Layers containing AcaSP and MMeT in the Paraloid B72 can be considered as stable over time compared to the evolution of the layer containing BTA, although this is the best protective layer within the first days of monitoring its effectiveness decreases over time reaching two ranks lower at the end of the monitoring period compared to the first day.

PUBLICATIONS AND SCIENTIFIC PROCEEDINGS LIST

Articles (ISI):

R. Bostan, S. Varvara, L. Găină, L. M. Mureşan, *Evaluation of some phenothiazine derivatives as corrosion inhibitors for bronze in weakly acidic solutio.* Corrosion. Science. 63, (**2012**), pg. 275-286, doi: 10.1016/j.corsci.2012.06.010,

IF= 4.16

S. Varvara, R. Bostan, L. Găină, L. M. Mureşan, *Thiadiazole as inhibitors for acidic media corrosion of artificially patinated bronze*, Materials and Corrosion, 65 (12), (**2014**) pg. 1202-1214, DOI: 10.1002/maco.201307072 **IF=1.4**

Articles (BDI):

S. Varvara, I. Rotaru, M. Popa, R. Bostan, M. Glevitzky,, L. M. Mureşan, *Environmentally-safe corrosion inhibitors for the protection of bronzes against corrosion in acidic media*, Chem. Bull. "POLITEHNICA" Univ. Timisoara, 55(69), 2, (**2010**), pg.156-161

Scientific communications:

R. Bostan, S. Varvara, A. Vlasa, L. M. Mureşan, *Carbon paste electrode for the study of patina originating from the surface of bronze artefacts,* 9th Spring Meeting of ISE, Turku (Finland), **May 2011**

R. Bostan, S. Varvara, L.. M.. Mureşan, E*valuation of some phenothiazine derivatives as environmentally friendly corrosion inhibitors for bronze in acidic solutions***,** 3rd Regional Symposium on Electrochemistry of South-East Europe, Bucharest, Romania, **May 2012**

R. Bostan, S. Varvara, L. M. Mureşan, *Thiadiazole derivatives as inhibitors for acidic media corrosion of artificially patinated bronze,* 4th Regional Symposium on Electrochemistry of South-East Europe, (RSE-SEE 4), Ljubljana, Slovenia, **May 2013**

SELECTIVE REFERENCES

[1]. M. Finšgar, I. Milošev, *Inhibition of copper corrosion by 1,2,3-benzotriazole: A review,* Corrosion Science, 52, **2010,** p 2737–2749.

[66]. E. Cano, D. Lafuente, D. M. Bastidas, *Use of EIS for the evaluation of the protective properties of coatings for metallic cultural heritage: A review*, Journal of Solid State Electrochemistry, 14, **2010**, p 381-391.

[80]. A. Dermaj, N. Hajjaji, S. Joiret, K. Rahmouni, A. Srhiri, H. Takenouti, V. Vivier, *Electrochemical and spectroscopic evidences of corrosion inhibition of bronze by a triazole derivative*, Electrochimica Acta, 52**, 2007**, p 4654-4662.

[84]. H. Saifi, M.C. Bernard, S. Joiret, K. Rahmouni, H. Takenouti, B. Talhi, *Corrosion inhibitive action of cysteine on Cu–30Ni alloy in aerated 0.5 M* H_2SO_4, Materials Chemistry and. Physis, 120**, 2010**, p 661- 669.

[85]. S. Varvara, L.M. Muresan, K. Rahmouni, H. Takenouti, *Evaluation of some nontoxic thiadiazole derivatives as bronze corrosion inhibitors in aqueous solution*, Corrosion Science, 50, **2008**, p 2596-2604.

[87]. M. Behpour, S.M. Ghoreishi, M. Salavati-Niasari, B. Ebrahimi, *Evaluating two new synthesized S–N Schiff bases on the corrosion of copper in 15% hydrochloric acid*, Materials Chemistry and. Physis, 107**, 2008**, p 153-157.

[105]. D.Q. Zhang, Q.R. Cai, L.X. Gao, K.Y. Lee, *Effect of serine, threonine and glutamic acid on the corrosion of copper in aerated hydrochloric acid solution*, Corrosion Science, 50, **2008**, p 3615-3621.

[107]. D.Q. Zhang, Q.R. Cai, X.M. He, L.X. Gao, G.S. Kim, *Corrosion inhibition and adsorption behavior of methionine on copper in HCl and synergistic effect of zinc ions*, Materials Chemistry and Physics, 114, **2009**, p 612-617.

[113]. H. Otmacic, E. E. Stupnišek-Lisac, *Copper corrosion inhibitors in near neutral media*, Electrochimica Acta, 48, **2003**, p 985-991.

[119]. K. Marusic, H. Otmacic-Curkovic, H. Takenouti, *Inhibiting effect of 4-methyl-1-p-tolylimidazole to the corrosion of bronze patinated in sulphate medium*, Electrochimica Acta, 56, **2011**, p 7491-7502.

[121]. L. Muresan, S. Varvara, E. Stupnišek-Lisac, H. Otmacic, K. Marusic, S. Horvat-Kurbegovic, L. Robbiola, K. Rahmouni, H. Takenouti, *Protection of bronze covered with patina by innoxious organic substances*, Electrochimica Acta, 52**, 2007**, p 7770-7779.

[161]. SPARTAN'06 Wavefunction, Inc., Irvine, CA.

[162]. D.J. Becke, *Density-functional thermochemistry III. The role of exact exchange*, Chemical Physics, 98, **1993**, p. 5648-5652.

[163]. C. Lee, W. Yang, R.G. Parr, *Development of the Colle–Salvetti correlation energy formula into a functional of the electron density*, Physical Review B 37, **1988**, p. 785-789.

[164]. P.J. Stephens, J. Devlin, C.F. Chabulowski, M.J. J Frisch, *Ab Initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields*, Journal of Physical Chemistry, 98, **1994**, p. 11623- 11627.

[168]. A.K. Singh, M.A. Quraishi, *The effect of some bis-thiadiazole derivatives on the corrosion of mild steel in hydrochloric acid*, Corrosion Science, 52, **2010**, p. 1373-1385.

[169]. I.D. Raistrick, J.R. MacDonald, D.R. Franceschetti, *The electrical analogs of physical and chemical processes*, in: J.R. MacDonald (Ed.), Impedance Spectroscopy Emphasizing Solid Materials and Systems, John Wiley & Sons, New York, **1987**.

[171]. K.F. Khaled, *Adsorption and inhibitive properties of a new synthesized guanidine derivative on corrosion of copper in 0.5 M* H_2SO_4, Applied Surface Science, 255, **2008**, p 1811-1818.

[177]. Y. M. Tang, W. Z. Yang, X. S. Yin, Y. Liu, R. Wan, J. T. Wang, *Phenyl-Substituted Amino Thiadiazoles as Corrosion Inhibitors for Copper in 0.5 M* H_2SO_4, Materials Chemistry and Physics, Vol. 116, No. 2-3, August **2009**, p. 479-483.

[178]. P. Bommersbach, C. Alemany-Dumont, J.P. Millet, B. Normand, *Formation and behaviour study of an environment-friendly corrosion inhibitor by electrochemical methods*, Electrochimica Acta, 51, **2005**, p 1076–1084.

[180]. K.M. Ismail, *Evaluation of cysteine as environmentally friendly corrosion inhibitor for copper in neutral and acidic chloride solutions*, Electrochimica Acta 52, **2007**, p 7811–7819.

[181]. P. Gupta, R.S. Chaudhary, T.K.G. Namboodhiri, B. Prakash, *Mechanism of dezincification and the inhibitive efficiency of some azoles for the corrosion of 70/30 brass in sulfuric acid*, British Corrosion Journal, 17, **1982**, p 136–141.

[187]. H. O. Curkovic´, T. Kosec, K. Marusic, A. Legat, *An electrochemical impedance study of the corrosion protection of artificially formed patinas on recent bronze*, Electrochimica Acta, 83, **2012**, p 28– 39.