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ORIGINAL ARTICLE

Study of the inhibition of the corrosion of copper and zinc in HNO_3 solution by electrochemical technique and quantum chemical calculations

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Abstract The corrosion inhibition of copper and zinc in 0.1 M HNO_3 by 1,2,3,4-tetrazole (TTZ) and some of its derivatives has been analysed in a comparative study. Two experimental techniques have been used such as weight-loss and electrochemical polarization measurements. The results obtained reveal that the addition of these compounds reduces preferentially the corrosion of Cu rather than that of Zn. The adsorption of tetrazolic compounds on a copper surface was more favourable than their adsorption on a zinc surface. Moreover the inhibition efficiency calculated for copper was found to attain 95% in the presence of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) while it remains constant at 1% for all compounds tested using zinc as electrode. Relationship between molecular structure and their inhibition efficiency was elucidated by quantum chemical calculations using the density functional theory (DFT).

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1. Introduction

The use of corrosion inhibitors increases continually (Popova et al., 1988; Kertit et al., 1998; Ye et al., 1998). The mechanism of their action can be different and depending on the metal, the medium and the structure of the inhibitor. One possible mechanism is the adsorption of the inhibitor, which protects the metal surface and thus does not permit the corrosion process to take place. We cite the heterocyclic compounds which act by their adsorption on the metal surface through their heteroatoms

such as sulphur, phosphorus, oxygen and nitrogen, double or triple bonds and aromatic rings (Mihit et al., 2006a,b; El Issami et al., 2005, 2002).

In some cases, the adsorption of the inhibitor molecules on the surface is weak and their presence in the corrosive solutions require maintaining the desired concentration of these agents to attain the minimal protection of the metal (Dafali et al., 2003; Zucchi et al., 2004; Carron et al., 1993). Other inhibitor molecules reduce the corrosion rate at limited immersion time and they must be continuously added to avoid the corrosion effect (Brunaro et al., 1992). Generally, it is found that some compounds inhibit the corrosion phenomenon while the others accelerate it (Gonzalez et al., 1993; Jennings and Laibinis, 1996; Refaey, 1996).

The mechanism of adsorption can be elucidated using quantum chemical methods (QCM). It is very useful to correlate the inhibitor molecular properties with its corrosion inhibition efficiency (Obot et al., 2009; Gece, 2008; Rayat et al., 2009). The properties include orbital energy, charge density and combined energy, etc.... Thus, QCM becomes a practical tool to get quantum chemical information to predict the inhibitory effect of such an inhibitor. Once a correlation between the structure and activity or property is found, any number of compounds, including those not yet synthesized, can be readily screened employing computational methodology and a set of mathematical equations which are capable of representing accurately the chemical phenomenon under study (Bentiss et al., 2004).

In our previous studies, we have focused more on the application of the azoles compounds and their derivatives as corrosion inhibitors for copper, zinc and their alloys in different media (Mihit et al., 2006a,b; El Issami et al., 2005, 2002). In this paper, we have also investigated in a comparative study the effect of the addition of some tetrazolic compounds on the corrosion inhibition of both copper and zinc in 0.1 M HNO_3. The experimental methods used for this study were the weight-loss and electrochemical polarization measurements.

2. Theoretical calculation

Quantum chemical calculations have been widely used to study reaction mechanisms and to interpret the experimental results as well as to resolve chemical ambiguities. The purpose of this work is to provide information about the electron configuration of several organic inhibitors (Fig. 1) by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency.

All the calculations were performed using the DFT/B3LYP functional (Lee et al., 1988; Becke, 1993) with a 6-31G* basis set. For this purpose the Gaussian 03 Quantum Chemistry Program (Frisch et al., 2004) with complete geometry optimisation was used. This computational method has been proven to yield satisfactory results. The easiest way to compare the inhibition efficiency of 1,2,3,4-tetrazole (TTZ), 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT), 1-phenyl-1,2,3,4-tetrazole (PT) and 5-amino-1,2,3,4-tetrazole (AT) is to analyse the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The optimised molecular structures are shown in Fig. 1 and the calculated energies E_{HOMO}, E_{LUMO}, ΔE (E_{LUMO}–E_{HOMO}) and other indices are given in Table 3 together with their inhibition efficiencies.

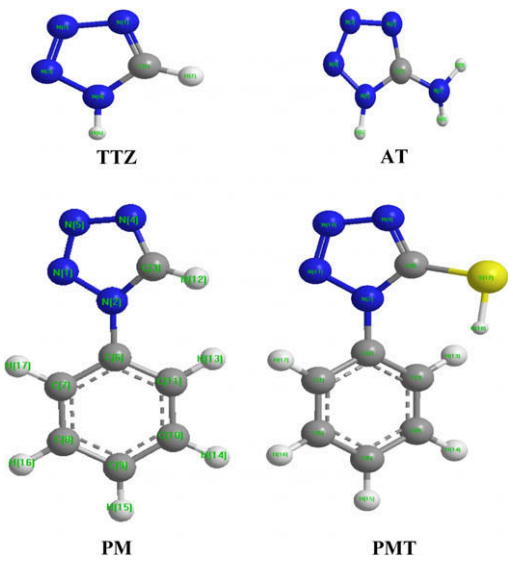

Figure 1 Molecular structures of the investigated substituted tetrazoles.

3. Experimental methods

The current–voltage characteristics are recorded with a potentiostat PGP 201, controlled by a computer. The scan rate is 60 mV/min and the potential is ranged from cathodic to anodic potentials. Before recording each curve, the working electrode is maintained with its free potential of corrosion. We used for all electrochemical tests a cell with three electrodes and double wall thermostats (Tacussel Standard CEC/TH). Saturated calomel (SCE) and platinum electrodes are used as reference and auxiliary electrodes, respectively. The composition of the working electrodes is given in Table 1.

Weight-loss tests were carried out in double distilled walled glass cell equipped with a thermostatic cooling condenser. The volume of the solution was 75 ml. Before each experiment, the surfaces of the specimens were polished with different emery papers up to 1200 grade, washed thoroughly with acetone, rinsed with distilled water and dried before being weighed and immersed in the corrosive solution. The corrosive solution 0.1 M HNO_3 was prepared by dilution of Analytical Grade 65% HNO_3 with distilled water. All experiments have been performed at a temperature of 25 ± 1 °C. The organic compounds: 1,2,3,4-tetrazole (TTZ), 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT), 1-phenyl-1,2,3,4-tetrazole (PT) and 5-amino-1,2,3,4-tetrazole (AT) tested as inhibitors are the ''Aldrich'' commercial products. Their molecular structures are shown in Fig. 1.

4. Results and discussion

4.1. Weight-loss measurements

The effect of the addition of tetrazolic compounds at 10^{-3} M on the corrosion of copper and zinc in 0.1 M HNO_3 solution was studied by using of weight-loss at 25 °C at 72 h of immersion duration (Table 2). The inhibition efficiency E_G (%) is calculated as follows:

Table 1 Chemical composition (in weight percent) of metals studied in working electrode.

Specimens	Cu	Zn	Fe	Sn	Al	Pb
Copper	99.9	0.04	0.03	–	0.03	–
Zinc	–	99.90	0.30	0.3	0.20	0.20

Table 2 Corrosion data of Cu and Zn in 0.1 M HNO_3 with and without tetrazoles at 10^{-3} M.

Solution	Copper		Zinc	
	W_{corr} (μg h^{-1} cm^{-2})	E_G (%)	W_{corr} (μg h^{-1} cm^{-2})	E_G (%)
Blank	3.6	–	720.6	–
TTZ	2.5	31	713.8	01
AT	1.5	58	710.5	01
PT	0.2	94	709.2	02
PMT	0.1	97	710.2	01

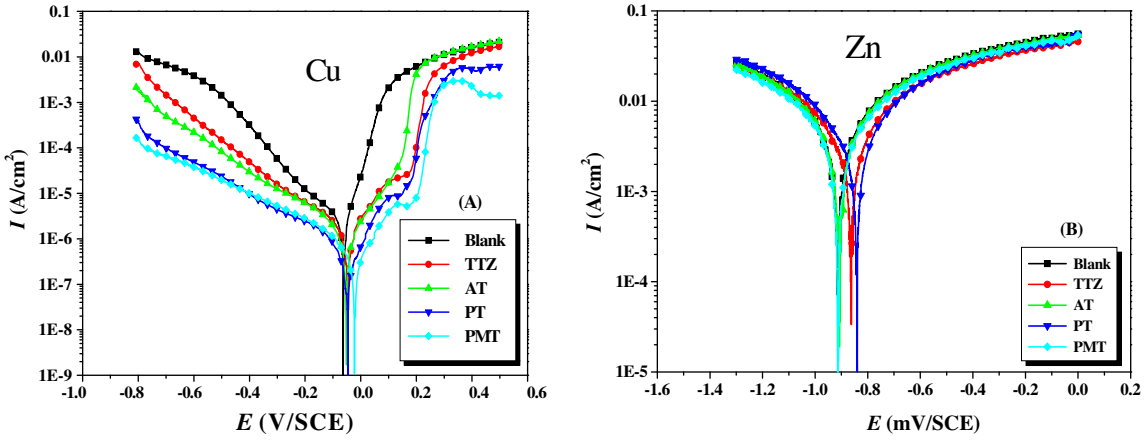

Figure 2 Polarization curves $I - E$ of: (A) copper and (B) zinc in 0.1 M HNO_3 with and without inhibitors at 10^{-3} M.

Table 3 Electrochemical parameters derived from Fig. 4(A) and (B).

Solution	Copper				Zinc			
	E_{corr} (mV/SCE)	I_{corr} (μA/cm^2)	β_c (mV/dec.)	E_I (%)	E_{corr} (mV/SCE)	I_{corr} (μA/cm^2)	β_c (mV/dec.)	E_I (%)
Blank	−63	4.3	−85	–	−914	1400	−110	–
TTZ	−49	3.0	−73	30	−871	1400	−110	0
AT	−54	1.7	−74	60	−911	1400	−110	0
PT	−51	0.3	−75	94	−850	1400	−110	0
PMT	−27	0.2	−75	95	−917	1400	−110	0

Table 4 The calculated quantum chemical parameters of the studied tetrazoles.

Parameter	TTZ	AT	PT	PMT
HOMO (eV)	−7.972	−6.956	−7.124	−7.052
LUMO (eV)	−0.632	−0.132	−1.373	−1.313
ΔE (eV)	7.340	6.824	5.751	5.739
$\mu\mu$ (Debye)	5.337	6.142	6.069	6.351
TE (eV)	−7024.4	−8530.2	−13309.1	−24139.7
Softness, σ (eV)	0.272	0.293	0.348	0.348
IE (%) (experimental result)	31	58	94	98

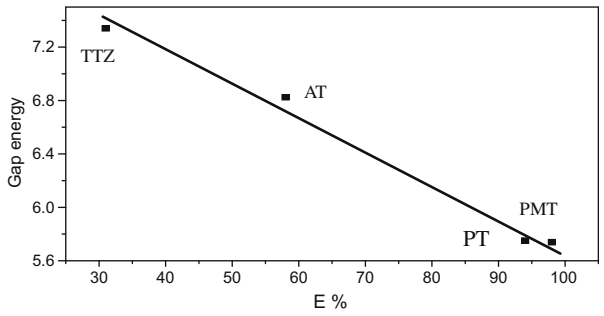

Figure 3 Correlation of gap energy and efficiency.

$$E_G\,(\%) = \left(1 - \frac{W'_{\text{corr}}}{W_{\text{corr}}}\right) \times 100 \qquad (1)$$

where W_{corr} and W'_{corr} are the corrosion rate of the metal in the absence and presence of inhibitor, respectively.

It is evident from the gravimetric results that the corrosion rate of zinc in the blank solution is higher than that of copper. Moreover, the addition of the organic compounds tested has no inhibition effect on the corrosion of zinc while it has reduced efficiently the corrosion process of copper. We suggested that the tetrazolic compounds has not been adsorbed on the zinc metal in nitric acid solution. In the case of copper, the inhibition efficiency was found to increase following the sequence: TTZ < AT < PT < PMT. This classification could be attributed to the nature of the substituents and their position. The

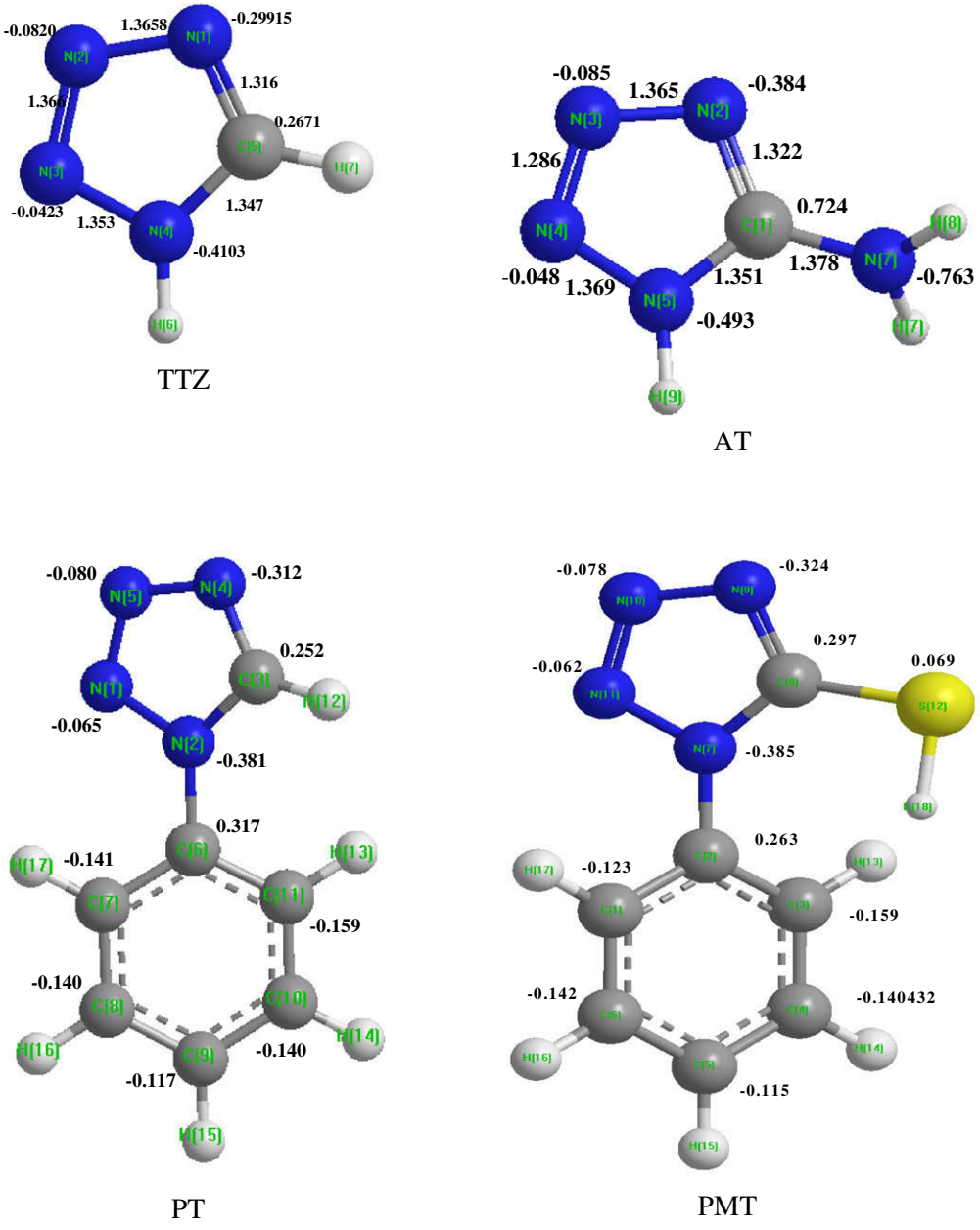

Figure 4 Optimised molecular structure of the inhibitor molecules: TTZ, AT, PT and PMT.

presence of NH_2 in AT, phenyl in PT, SH_2 and phenyl in PMT may increase the polarity and the adsorbability of the inhibitors on the metal surface. The presence of electron donor groups (N, S, and aromatic ring), the free electron pairs in the sulphur and nitrogen atoms and π electrons on aromatic nuclei in the molecular structure of PMT favours its adsorption on the copper surface. Consequently, its inhibition efficiency reached a maximum value 97%. Similar results have been obtained with PMT for a copper (Mihit et al., 2008) and either copper and a 60Cu40Zn alloy in 0.1 M HNO_3 (Mihit et al., 2006a,b).

4.2. Electrochemical measurements

Fig. 2(A) and (B) illustrates, respectively, the polarization curves of copper and zinc in 0.1 M HNO_3 with and without the addition of tetrazolic compounds at 10^{-3} M. The corresponding electrochemical parameters are reported in Table 3. The inhibition efficiency values were calculated according to Eq. (2):

$$E_I\ (\%) = \left(1 - \frac{I'_{corr}}{I_{corr}}\right) \times 100 \qquad (2)$$

where I_{corr} and I'_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively, determined by extrapolation of cathodic Tafel lines towards E_{corr}.

According to Fig. 2(A) and associated parameters, it is shown that the addition of the inhibitors reduce efficiently both cathodic and anodic current density indicating that the tetrazole compounds act as mixed-type inhibitors toward copper. On the other hand, the linear plots of cathodic Tafel lines indicate that the hydrogen evolution reaction is activation controlled. The corrosion current density was found to decrease in the presence of the inhibitors accompanied by an increase of the inhibition efficiency values following the same order obtained before.

According to Fig. 2(B) and associated parameters (Table 3), the presence of tetrazolic inhibitors has not affected the shape of the polarization curves. Consequently, cathodic, anodic and corrosion current densities and Tafel slopes are unchanged. These results indicate that the tetrazole compounds have no inhibition activity on zinc, which can be explained by the absence of the adsorption phenomena of these molecules through their heteroatoms on the zinc surface. The electrochemical method confirms the results obtained by the weight-loss technique.

4.3. Prediction of theoretical parameters

According to Fukui's frontier molecular orbital theory (Fujiimoto et al., 1974), the reactive ability of the inhibitor is related with the frontier molecular orbitals (MO) that are the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO. Higher HOMO energy (E_{HOMO}) of the adsorbent leads to higher electron donating ability (Lee et al., 1988). Low LUMO energy (E_{LUMO}) indicates that the acceptor accepts electrons easily. The calculated quantum chemical indices (E_{HOMO}, E_{LUMO} and the dipole moment μ of PMT, PT, TTZ and AT are shown in Table 4.

The difference $\Delta E = E_{LUMO} - E_{HOMO}$ is the energy required to move an electron from HOMO to LUMO. According to the work of Issa et al. (2008), a low ΔE facilitates adsorption of the molecule and thus will cause higher inhibition efficiency.

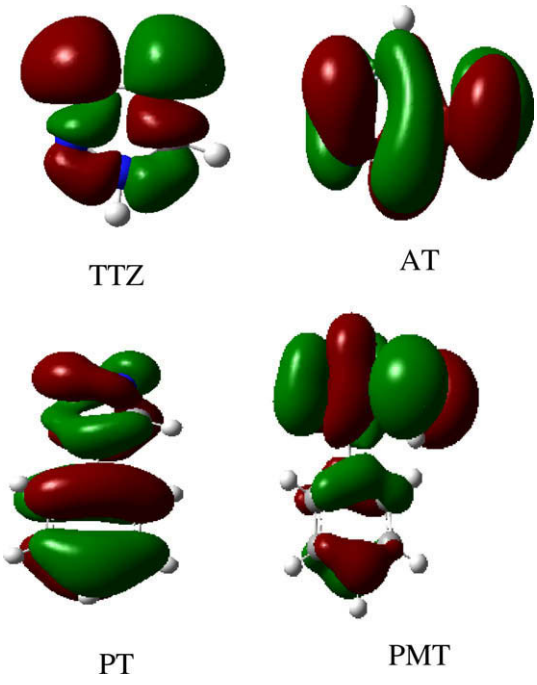

Figure 5 Highest occupied molecular orbital (HOMO) of TTZ, AT, PT and PMT.

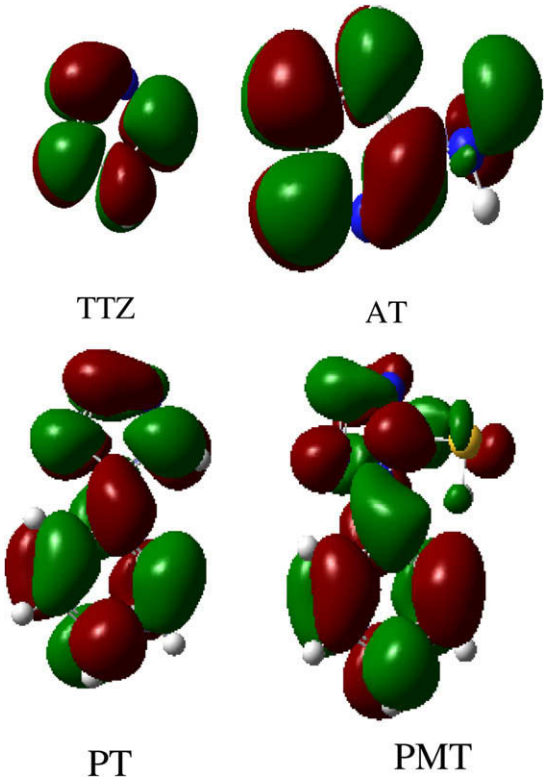

Figure 6 Lowest unoccupied molecular orbital (LUMO) of TTZ, AT, PT and PMT.

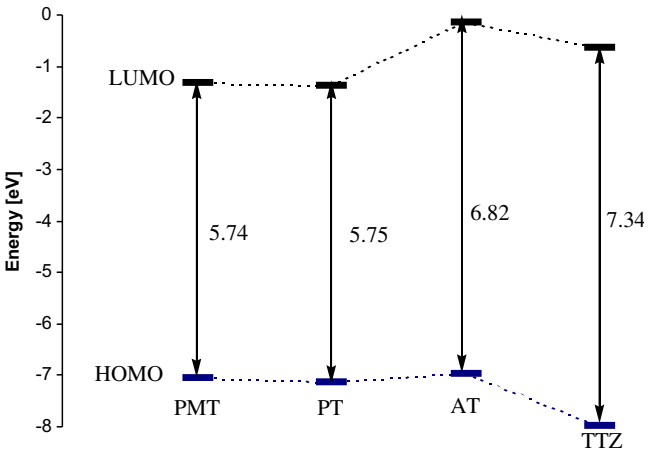

Figure 7 Relation between frontier molecular orbitals of TTZ, AT, PT and PMT and their gap energy.

The band gap energy ΔE increases from PMT over PT and AT to TTZ. This fact explains the decreasing inhibition efficiency in this order as shown in Table 4 and in Fig. 3. Fig. 4 shows the optimised structures of the four compounds studied. Table 4 also indicates that PMT possesses the lowest total energy that means that PMT adsorption occurs easily and is favoured by the highest softness. It can be seen that the substitution of hydrogen atoms by phenyl and sulphur leads to a higher inhibition and all calculated quantum chemical parameters validate these experimental results.

The HOMO and LUMO electronic density distributions of these molecules (PMT, PT, TTZ, and AT) were plotted in Figs. 5 and 6. For the HOMO of the studied compounds, it can be observed that the benzene ring, –C═N– and the substituent on the tetrazole (NH_2 and SH) have a large electron density. Fig. 7 shows the size and position of the HOMO–LUMO gap. Even though the total charge on all the molecules is zero, the nature of chemical bonds is such that the positive and negative charges do not completely overlap in most molecules. Such molecules are said to be polar because they possess a permanent dipole moment. The data presented in Table 4 shows that the calculated dipole moment increases from TTZ over AT and PT to PMT with the substitution of hydrogen atoms by a phenyl group and a sulphur atom, respectively. PMT has the highest dipolar moment and consequently the reactivity of the molecule on the surface is hugely facilitated. More information should be given by the calculation of the total energy (Table 4). Hohenberg and Kohn (1964) stated that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The lower TE is estimated to PMT which exhibited the highest inhibition efficiency.

5. Conclusion

From the obtained results, we can deduce the following conclusions:

- Tetrazole compounds were found to be effective as corrosion inhibitors on pure copper in nitric acid solution but did not affect the kinetic process of pure zinc.
- The inhibition efficiency improves with the increase of inhibitor concentration and follows the sequence: TTZ < AT < PT < PMT.
- Electrochemical measurements revealed that tetrazoles act as mixed-type inhibitors on copper in acid solution.
- Through DFT quantum chemical calculations a correlation between parameters related to the electronic structure of tetrazolic compounds and their ability to inhibit the corrosion process could be established. The calculated energy gaps show reasonably good correlation with the efficiency of corrosion inhibition.

References

Becke, A.D., 1993. J. Chem. Phys. 98, 5648.
Bentiss, F., Traisnel, M., Vezin, H., Hildebrand, H.F., Lagrenée, M., 2004. Corros. Sci. 46, 2781.
Brunaro, G., Parrmigiani, F., Perboni, G., Rocchini, G., Trabanelli, G., 1992. Br. Corros. J. 27, 75.
Carron, K.T., Lowis, M.L., Dong, J., Ding, J., Xue, G., Chen, Y., 1993. J. Mater. Sci. 28, 4099.
Dafali, A., Hammouti, B., Mokhlisse, R., Kertit, S., 2003. Corros. Sci. 45, 1619.
El Issami, S., Bazzi, L., Hilali, R., Salghi, S., Kertit, S., 2002. Ann. Chim. Sci. Mat. 27, 63.
El Issami, S., Mihit, M., Bazzi, L., Salghi, R., Hilali, M., Ait Addi, E., 2005. Trans. SAEST 40, 24.
Frisch, M.J. et al., 2004. Gaussian 03, Revision B.05. Gaussian, Inc., Wallingford, CT.
Fujiimoto, H., Yamabe, S., Fukui, K., 1974. J. Chem. Phys. 60, 572.
Gece, G., 2008. Corros. Sci. 50, 2981.
Gonzalez, S., Laz, M.M., Souto, R.M., Salvarezza, R.C., Arvia, A.J., 1993. Corrosion 49, 450.
Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. Phys. Rev. 136, B864.
Issa, R.M., Awad, M.K., Atlam, F.M., 2008. Appl. Surf. Sci. 255, 2433.
Jennings, G.K., Laibinis, P.E., 1996. Physicochem. Eng. Asp. 116, 105.
Kertit, S., Es-Soufi, H., Hammouti, B., Benkaddour, M., 1998. J. Chim. Phys. 95, 2070.
Lee, C., Yang, W., Parr, R.G., 1988. Phys. Rev. B 37, 785.
Mihit, M., El Issami, S., Bouklah, M., Bazzi, L., Hammouti, B., Ait Addi, E., Salghi, R., Kertit, S., 2006a. Appl. Surf. Sci. 252, 2389.
Mihit, M., Salghi, R., El Issami, S., Bazzi, L., Hammouti, B., Ait Addi, E., Kertit, S., 2006b. Pigment Resin Technol 35, 151.
Mihit, M., Bazzi, L., Salghi, R., Hammouti, B., El Issami, S., Ait Addi, E.H., 2008. Int. Scient. J. Alternat. Energ. Ecol. 6, 173.
Obot, I.B., Obi-Egbedi, N.O., Umoren, S.A., 2009. Corros. Sci. 51, 276.
Popova, A., Sokolova, E., Raicheva, S., 1988. Khim. -Ind. 60, 72.
Rayat, S., Chhabra, R., Alawode, O., Gundugola, A.S., 2009. J. Mol. Struct. 933, 38.
Refaey, S.A.M., 1996. J. Appl. Electrochem. 26, 503.
Ye, X.R., Xin, X.Q., Zhu, J.J., Xue, Z.L., 1998. Appl. Surf. Sci. 135, 307.
Zucchi, F., Grassi, V., Frignani, A., Trabanelli, G., 2004. Corros. Sci. 46, 2853.