The Quantum Chemical Calculations of Some Thiazole Derivatives

Murat Saracoglu[1*], Fatma Kandemirli[2], Mohammed A. Amin[3,4], Can Dogan Vurdu[2], Muhammet Serdar Cavus[2], Gokhan Sayıner[5]

[1]*Faculty of Education, Erciyes University, 38039 Kayseri, Turkey*
[2]*Biomedical Engineering Department, Faculty of Engineering and Architecture, Kastamonu University, 37200, Kastamonu, Turkey*
[3]*Materials and Corrosion Lab (MCL), Department of Chemistry, Faculty of Science, Taif University, 888 Hawaiya, Taif, Saudia Arabia*
[4]*Department of Chemistry, Faculty of Science, Ain Shams University, 11566 Abbassia, Cairo, Egypt*
[5]*Gebze Enstitute of Tecnology, Faculty of Engineering, 41400, Kocaeli, Turkey*

Received: 28 September 2014 / Accepted: 30 November 2014

Abstract:
An examination of quantum chemical and corrosion inhibition studies for some thiazole derivatives, namely 2-amino-4-(p-tolyl)thiazole (APT), 2-methoxy-1,3-thiazole (MTT) and thiazole-4-carboxaldehyde (TCA) had been tested as corrosion safe inhibitors for mild steel (CRS) in 0.5 M H2SO4 solutions at 25 °C temperature. The correlation between inhibition efficiency and descriptor variables obtained from the quantum chemical calculation using B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p), and CBS-APNO methods. Result showed that APT could have better performance as corrosion inhibitor for the non-protonated and protonated for gas and solvent phase compounds using CBS-Q method. The results of the highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{LUMO} and E_{HOMO} (ΔE), dipole moments (DM), molecular volume (MV), sum of the total negative charge (TNC), global hardness (η), softness (σ), electronegativity (χ), chemical potential (μ), Global Electrophilicity (ω) and sum of electronic and zero-point energies (SEZPE) of three methods are compatible with each other very well.

Key words: *B3LYP, CBS-APNO, corrosion inhibition, mild stell, quantum chemical calculations, thiazole derivatives*

Introduction

There are several quantum-chemistry studies performed in order to relate the inhibition efficiency to the molecular properties of the different types of compounds. Kandemirli et al investigated computational simulations of the molecular structure and corrosion properties examination of quantum chemical and corrosion inhibition studies for three serine (Ser), therionine (Thr) and glutamine (Glu) which had been tested as corrosion safe inhibitors for cold rolled steel (CRS) in 1.0 M HCl solutions at different temperatures (283-333 K) were made to see if any clear links exist between them in both, gaseous phase and solvent phase as non-protonated and protonated compounds, indicated that all inhibitor systems have a very similar capacity for charge donation, since the values of E_{HOMO} presented a small difference between them [1]. Hongfang Ma et al [2] revealed that the inhibition efficiency has certain relationship to highest occupied molecular orbital (HOMO) energy and the combined energy between the pyridine–pyrazole inhibitor molecules and the iron atom. Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides [3] thiosemicarbazones [4], benzamide (BA) and 4-aminobenzene sulfonamide (ABSA) [5], qualine derivatives [6], amino acids, namely, serine (Ser), threonine (Thr), and glutamine (Glu) [7], piperidine and these derivatives [8] triazole Schiff bases [9], Aminic nitrogen-bearing polydentate Schiff base compounds [10], have been performed.

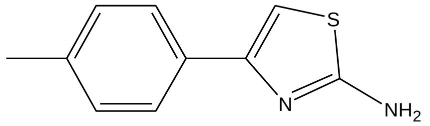
In this paper, we have studied a detailed quantum chemical calculations of some thiazole derivatives, namely 2-amino-4-(p-tolyl)thiazole (APT), 2-methoxy-1,3-thiazole (MTT) and thiazole-4-carboxaldehyde (TCA) (Figure 1) [11].

Full geometrical optimizations of the APT, MTT and TCA molecules were performed by using the density functional theory (DFT) with the Beck's three parameter exchange functional along with the Lee-Yang-Parr non-local correlation functional (B3LYP) [12-14] with 6-311G(d,p), 6-311++G(2d,2p) basis sets of and by using the quadratic complete basis set (CBS-Q) calculation method for neutral and protonated forms in the gas phase and in the presence of solvent implemented in Gaussian 03 (revision D.01) package [15].

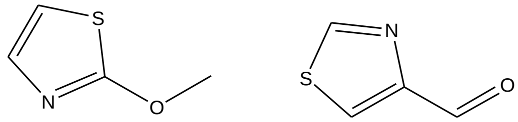
***Corresponding author:** Murat Saracoglu,
E-mail: muratsaracoglu@gmail.com

Experimental

The molecular sketches of the compounds were drawn using the GaussView 5.0. DFT calculations were carried out by using B3LYP/6-311G(d,p), B3LYP/6-311G++(2d,2p) and by using the quadratic complete basis set (CBS-Q) calculation method with the GAUSSIAN 03 computational package program. Geometry optimization is carried out at the B3LYP/6-311G++(2d,2p).



2-Amino-4-(p-tolyl)thiazole (APT)



2-Methoxy-1,3-thiazole (MTT) Thiazole-4-carboxaldehyde (TCA)

Figure 1. The chemical structures of the molecules investigated.

In this study, the highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{HOMO} and E_{LUMO} (ΔE), dipole moments (DM), molecular volume (MV), sum of the total negative charge (TNC), global hardness (η), softness (σ), chemical potential (μ), electronegativity (χ), Global Electrophilicity (ω) and sum of electronic and zero-point energies (SEZPE) have been calculated with a detailed quantum chemical study.

Molecular properties, related to the reactivity and selectivity of the compounds, were estimated following the Koopmans's theorem relating the energy of the HOMO and the LUMO.

Koopmans theorem, the chemical potential (μ) and hardness (η) values measures the resistance of an atom to a charge transfer can be approximated in terms of the energies of the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}):

$$\mu \cong -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \quad (1)$$

$$\eta \cong -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \quad (2)$$

The inverse of the hardness is expressed as the global softness (σ),

$$\sigma = \frac{1}{\eta} \quad (3)$$

The electronegativity (χ) is estimated by using the equation:

$$\chi \cong \frac{1}{2}(E_{HOMO} + E_{LUMO}) \quad (4)$$

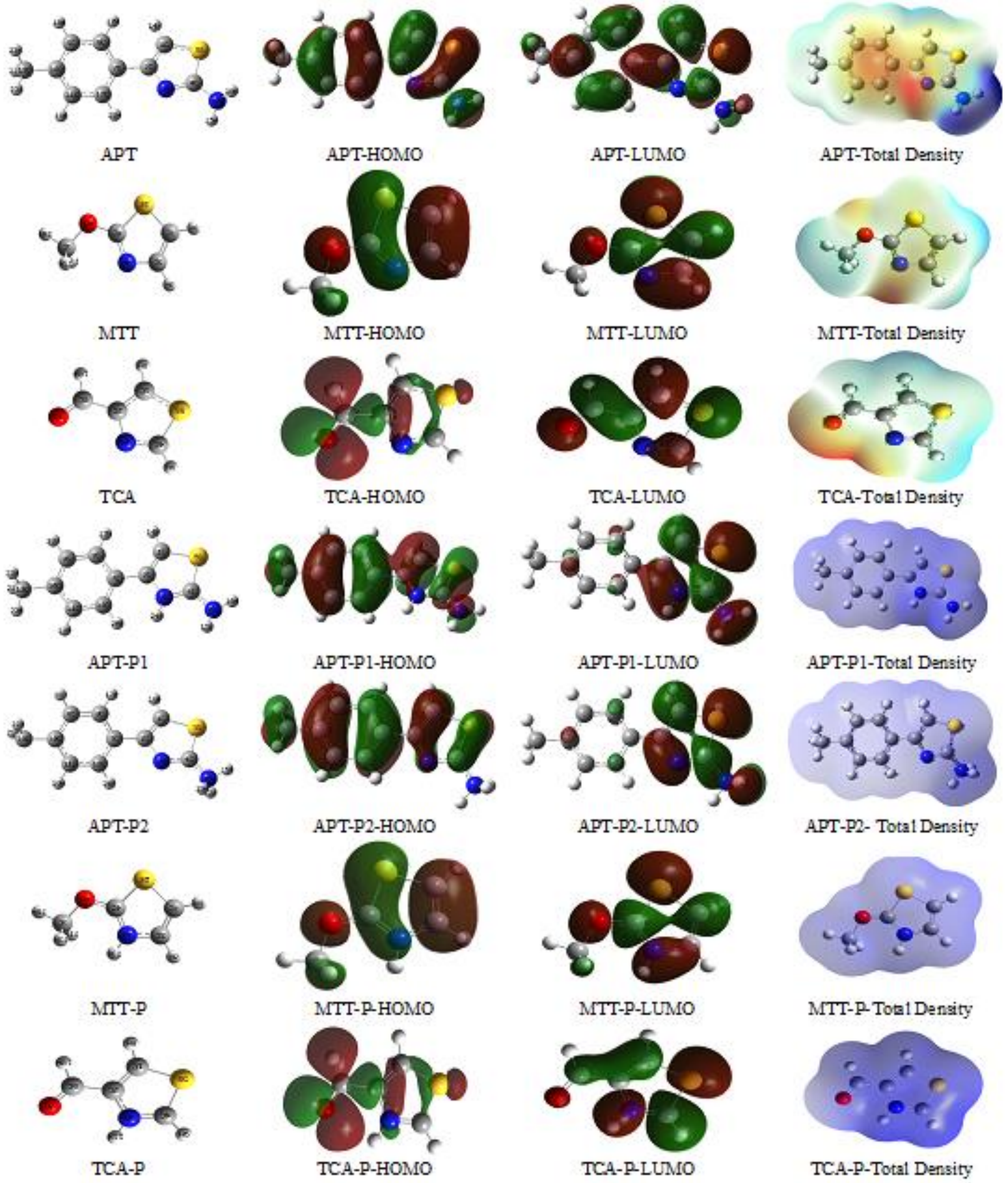
Results and Discussion

The optimized structure, Frontier molecular orbitals and together with the total electron density, electron population of some thiazole derivatives, APT, MTT and TCA are given for the non-protonated and protonated compounds in Figure 2.

DFT takes into account a part of correlation and it has been reported to provide fairly good results for the description of various molecular properties such as the energy of the Highest Occupied Molecular Orbital (HOMO), the energy of the Lowest Unoccupied Molecular orbital (LUMO), electronegativity (χ), etc. (Figure 3).

In the present study, DFT in combination with the B3LYP functional and CBS-APNO were utilized in order to compare the effect of the different functionals on the calculated molecular properties for the systems under study. DFT/B3LYP and CBS-APNO were been widely used in the description of the chemical reactivity and selectivity of molecules.

In MO terms, the most important states are those in which an electron is promoted from a filled MO to an empty MO. For molecular reactions, the important states are those in which electrons are promoted from filled MO's in one reactant to empty MO's in the other. In simple MO theory the HOMO and the LUMO defining the lowest energy transition are the orbitals that drive the chemical reaction. When a molecule is treated as formed by the combination of two fragments; the fragment that acts as a Lewis base (an electron pair donor) supplies the electrons from it's HOMO, and the fragment that acts as a Lewis acid (an electron air acceptor) accommodates the incoming electrons. So the energy of the lowest unoccupied molecular orbital (E_{LUMO}) indicates the ability of accepting electrons to molecule and high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with empty molecular orbitals.



APT APT-HOMO APT-LUMO APT-Total Density

MTT MTT-HOMO MTT-LUMO MTT-Total Density

TCA TCA-HOMO TCA-LUMO TCA-Total Density

APT-P1 APT-P1-HOMO APT-P1-LUMO APT-P1-Total Density

APT-P2 APT-P2-HOMO APT-P2-LUMO APT-P2- Total Density

MTT-P MTT-P-HOMO MTT-P-LUMO MTT-P-Total Density

TCA-P TCA-P-HOMO TCA-P-LUMO TCA-P-Total Density

Figure 2. The optimized molecular structures, HOMO, LUMO and total density of the gas phase and gas phase with protonated inhibitor molecules using DFT/B3LYP/6-311++G(2d,2p).

The highest energy occupied molecular orbital called HOMO and the lowest energy unoccupied molecular orbital called LUMO are the most important orbitals that interact each other in the molecular interaction. The HOMO for APT, APT-P1, APT-P2 is delocalized over benzene ring and thiazole ring and LUMO for ATP is delocalized over benzene ring and thiazole ring, while for APT-P1, APT-P2 is delocalized over thiazole ring. HOMO and LUMO orbital for MTT is delocalized mainly thiazole ring. For TCA HOMO orbital is localized over C=O group and LUMO is delocalized over whole molecule. The calculated E_{HOMO} values of APT, MTT and TCA for B3LYP/6-311G(d,p) are –5.54, –6.27, and, –7.44 eV, respectively (Figure 3).

The calculated highest occupied molecular orbital energy and lowest unoccupied molecular orbital energy and energy gab between them for the APT, MTT, TCA and protonated form of them in gas and solvent phase and the experimental corrosion inhibition efficiency (%IE) for APT, MTT, TCA are represented in Figure 3.

As seen from the Figure 3, E_{HOMO} value of APT, MTT, TCA calculated by CBS-Q are –7,640 eV, and –8,748 eV, –9,858 eV in gas phase, and –7,811, –8,813 and –9,626 eV in water. Higher values of E_{HOMO} indicate better tendency towards the donation of electron to the metal surface. The order of the experimental %IE obtained in this study is 2-Amino-4-(p-tolyl)thiazole (APT) > 2-Methoxy-1,3-thiazole (MTT) > Thiazole-4-carboxaldehyde (TCA).

The metal ion can donate electrons in its d-orbitals to the empty orbital of the inhibitor molecules and can lead the formation of a feedback bond. The lower value of E_{LUMO} indicates the better back donation and the better inhibition efficiency. The value of E_{LUMO} calculated is in the order APT < MTT < TCA which supports the order obtained for the inhibition efficiencies (Figure 3).

The HOMO-LUMO energy gap (ΔE) is effective on chemical reactivity. So there must be a relationship with corrosion inhibition mechanism. Hardness and softness are the basic chemical concepts, called global reactivity descriptors and has been theoretically justified within the framework of density functional theory (DFT) [16, 17]. These are the important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [3, 17]. A low energy gap is generally associated with the high chemical activity. In our present study APT with low hardness values 4.35, 4.46, 4.06 and 4.69 (eV) compared with other compounds the non-protonated and protonated for gas and solvent phase compounds using CBS-Q method, respectively. Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency [17, 18]. The softness value for APT of, 0.23 eV–1, has the highest inhibition efficiency for gas phase using CBS-Q method (Figure 4).

In the studied molecules, the trend for the energy gap values have the order TCA > MTT > APT calculated by the CBS-Q method, so APT has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor. The energy gap (ΔE) was found 10.76, 9.84 and 8.71 for TCA, MTT and APT CBS-Q methods for neutral molecules at the gas phase and 10.91, 9.98 and 8.92 for solvent phase TCA, MTT and APT using CBS-Q, respectively. Similarly, The energy gap (ΔE) was found TCA > MTT > APT by the CBS-Q method for protonated compounds at gas and solvent phase (Figure 4).

The results show that electronegativity (χ) of studied molecules are with the order of TCA > MTT > APT with the calculation B3LYP/6-311G(d,p). According to Sanderson's electronegativity equalization principle [19], TCA with a high electronegativity and low difference of electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency.

As shown in Figures 3 and 4, the results of the highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{LUMO} and E_{HOMO} (ΔE), dipole moments (DM), molecular volume (MV), sum of the total negative charge (TNC), global hardness (η), softness (σ), electronegativity (χ), chemical potential (μ), Global Electrophilicity (ω) and sum of electronic and zero-point energies (SEZPE) of three methods are compatible with each other very well.

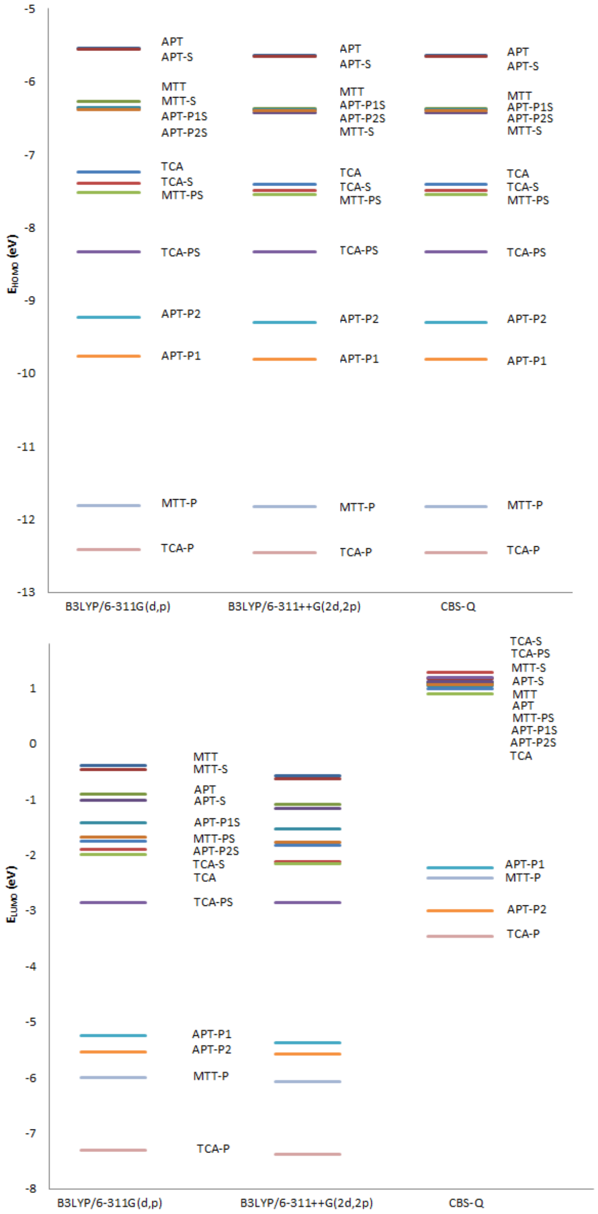


Figure 3. The calculated HOMO and LUMO energy values for the non-protonated and protonated for gas and solvent phase compounds using B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p) and CBS-Q methods.

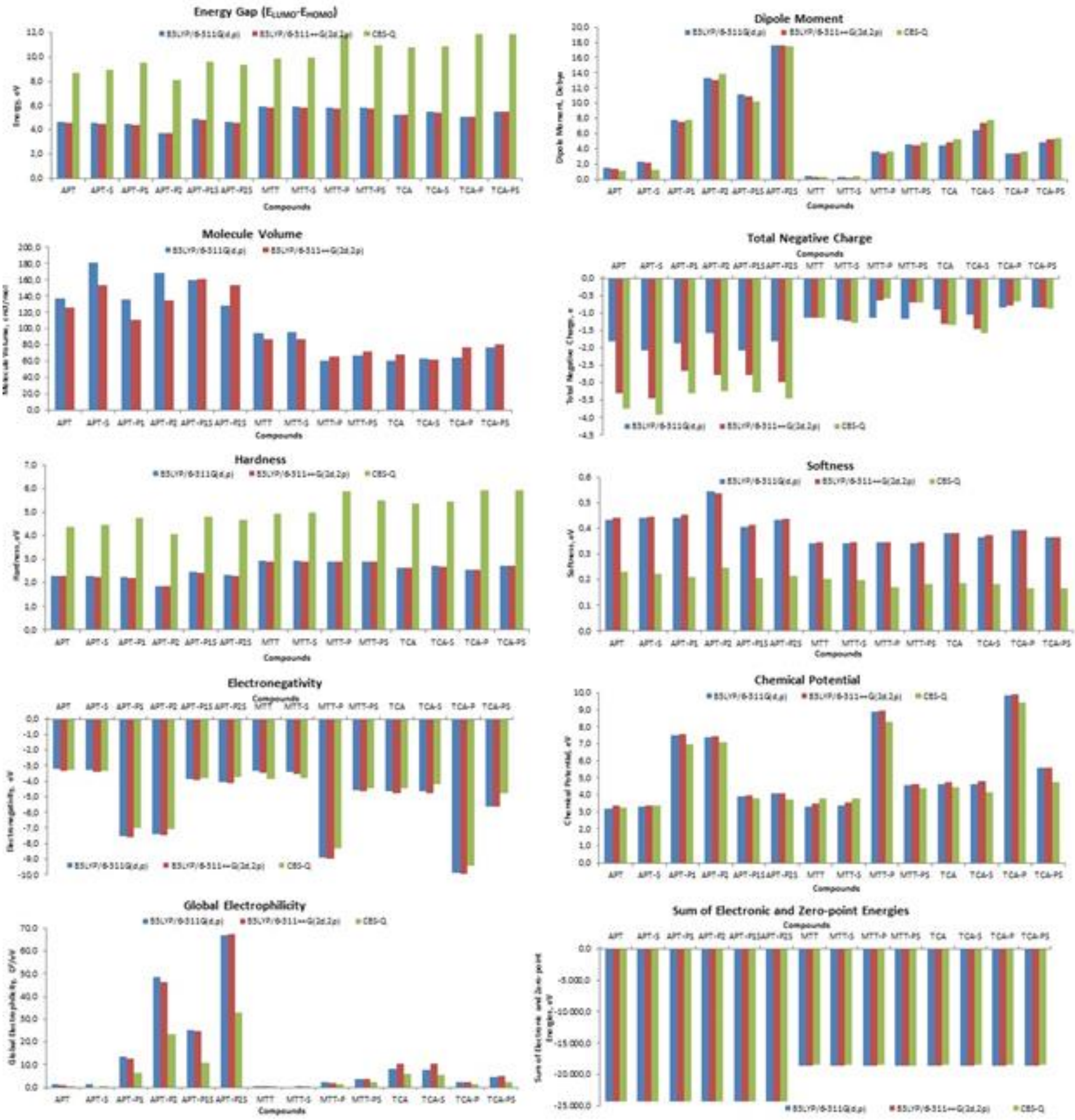


Figure 4. The calculated quantum chemical parameters for the non-protonated and protonated for gas and solvent phase compounds using B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p) and CBS-Q methods.

Conclusions

APT could have better performance as corrosion inhibitor for the non-protonated and protonated for gas and solvent phase compounds using CBS-Q method.

Quantum chemical descriptors such as E_{HOMO}, E_{LUMO}, the energy gap between E_{HOMO} and E_{LUMO}, dipole moments, molecular volume, sum of the total negative charge, global hardness, softness, electronegativity, chemical potential, global electrophilicity, and sum of electronic and zero-point energies were calculated and showed compatibility to each other.

References

[1] F. Kandemirli, M. Saracoglu, M. A. Amin, M. A. Basaran, and C. D. Vurdu, The Quantum chemical calculations of serine, therionine and glutamine, *Int. J. Electrochem. Sci.*, **9**(7), 2014, 3819-3827.

[2] H. Ma, S. Chen, Z. Liu and Y. Sun, Theoretical elucidation on the inhibition mechanism of pyridine–pyrazole compound: A Hartree Fock study, *J. Mol. Struct. (Theochem)*, **774**(1-3), 2006, 19-22.

[3] J. Fang and J. Li, Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides, *J. Mol. Struct. (Theochem)*, **593**(1-3), 2002, 179-185.

[4] F. Kandemirli and S. Sagdinc, Theoretical study of corrosion inhibition of amides and thiosemicarbazones, *Corros. Sci.*, **49**(5), 2007, 2118-2130.

[5] S. Zor, M. Saracoglu, F. Kandemirli and T. Arslan, Inhibition effects of amides on the corrosion of copper in 1.0 M HCl: Theoretical and experimental studies, *Corros.*, **67**(12), 2011, 125003 (11 pages).

[6] E. E. Ebenso, M. M. Kabanda, T. Arslan, M. Saracoglu, F. Kandemirli, L. C. Murulana, A. K. Singh, S. K. Shukla, B. Hammouti, K. F. Khaled, M. A. Quraishi, I. B. Obot, and N. O. Edd, Quantum chemical investigations on quinoline derivatives as effective corrosion inhibitors for mild steel in acidic medium, **7**(6), 2012, 5643-5676.

[7] M. A. Amin, O. A. Hazzazi, F. Kandemirli, and M. Saracoglu, Inhibition performance and adsorptive behaviour of three amino acids on cold rolled steel in 1.0 M HCl-chemical, electrochemical and morphological studies, *Corros*, **68**(8), 2012, 688-698.

[8] K. F. Khaled, K. Babi´-Samardžija, and N. Hackerman, Piperidines as corrosion inhibitors for iron in hydrochloric acid, *J. Appl. Electrochem.*, **34**(7), 697-704.

[9] M. K. Awad, R. M. Issa and F.M. Atlam, Theoretical investigation of the inhibition of corrosion by some triazole Schiff bases, Mater. *Corros.*, **60**(10), 2009, 813-819.

[10] H. Ju, Z. P. Kai and Y. Li, Aminic nitrogen-bearing polydentate Schiff base compounds as corrosion inhibitors for iron in acidic media: A quantum chemical calculation, *Corr. Sci.*, **50**(3), 2008, 865-871.

[11] K. F. Khaled, M. A. Amin, Corrosion monitoring of mild steel in sulphuric acid solutions in presence of some thiazole derivatives – Molecular dynamics, chemical and electrochemical studies, *Corr. Sci.*, **51**(9), 2009, 1964-1975.

[12] A. D. Becke, A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.*, **98**(2), 1993, 5648-5652.

[13] C. Lee, W. Yang and R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev B.*, **37**(2), 1988, 785-789.

[14] P.J. Stevens, F.J. Devlin, C.F. Chablowski, and M.J. Frisch, Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields, *J. Phys. Chem.*, **98**(45), 1994, 11623-11627.

[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision D.01, Gaussian Inc., Wallingford CT, 2004.

[16] P. Hohenberg and W. Kohn, Inhomogeneous Electron Gas, *Phys. Rev.*, **136**(3B), 1964, B864-B871.

[17] P. Udhayakala, A.M. Samuel, T.V. Rajendiran, and S. Gunasekaran, DFT study on the adsorption mechanism of some phenyltetrazole substituted compounds as effective corrosion inhibitors for mild steel, *Der Pharma Chemica*, **5**(6), 2013, 111-124.

[18] E. E. Ebenso, D. A. Isabirye, and N. O. Eddy, Adsorption and quantum chemical studies on the inhibition potentials of some thiosemicarbazides for the corrosion of mild steel in acidic medium, *Int. J. Mol. Sci.*, **11**(6), 2010, 2473-2498.

[19] P. Geerlings and F. De Proft, Chemical reactivity as described by quantum chemical methods, *Int. J. Mol. Sci.*, **3**, 2002, 276-309.