Proceeding of 2nd International Science Postgraduate Conference 2014 (ISPC2014)

Predictive Model of 2-cyclohexylthiophene for corrosion inhibition in mild steel using Computational Method.

Bishir Usman[1,2], Hasmerya Maarof[1], Hassan H. Abdallah[1,3], Rosmahaida Jamaludin[1], Abdo M. Al-Fakih[1,4], Madzlan Aziz[1*]

[1]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Johor Darul Ta'azim, Malaysia
[2]Department of Pure and Industrial Chemistry, Faculty of Science, Bayero University, Kano. P. M. B. 3011, Kano, Nigeria.
[4]Department of Chemistry, Education College, Salahaddin University, Erbil, Iraq.

[4]Department of Chemistry, Faculty of science, Sana'a University, Sana'a, Yemen
[*1] madzlan@utm.my;[2] bishirbum@yahoo.com

Abstract: Corrosion inhibition activity of 2-cyclohexylthiophene (2CHT) for mild steel in acidic media was predicted using QSAR tool. The model used two descriptors namely; Moran autocorrelation of lag4 weighted by mass (MATS4M) which explained the linearity and branching of the compounds and largest eigen values n3 of burden matrix weighted by mass (SPMAX3-Bh(m)) describes the nature and size of the neighboring atom. The modeling results revealed the potential of the compounds as a good corrosion inhibitor with percentage inhibition efficiency (%IE) of 76.5%. Quantum chemical calculation using DFT with 6-311G++(d,p) basis was used to evaluate the performance of the predicted compound as corrosion inhibitor by quantum chemical parameters such as E_{HUMO}, E_{LUMO}, Energy gap (E_{gap}), hardness (η), softness (S), dipole moment (μ), electronegativity (X), electron affinity (A), ionization energy (I) and total energy (TE). The results obtained from quantum chemical parameters were found to be consistent with predicted result.

Keywords ; Corrosion Inhibtion, QSAR, 2-cyclohexylthiophene, DFT calculation

1.0 Introduction

Organic corrosion inhibitors are the most widely used inhibitors in corrosion protection for fast few years. Organic compounds containing hetero atoms such as N, O, S and P were found to be promising in reducing corrosion damage [1]. The mechanism of corrosion inhibition of the metal surface in acidic media can best be explained by ability of the inhibitor to be adsorbed onto the metal surface which acts as a barrier against reaction to continue [2]. The presence of functional groups that are electron sufficient, pi-electron and lone pair of electron are the other important structural features facilitating the adsorption activity of the inhibitor [3,4].

Many studies have been reported extensively on effect of heterocyclic compounds containing N, O and S, as corrosion inhibitors [5-11].

Nowadays the use of theoretical chemistry has become very popular in predicting corrosion inhibition with the introduction of developmental computational hardware with efficient algorithm that can be used in molecular quantum mechanical calculations [12]. Quantitative Structure activity relationship is the mathematical relationship established between the property of a chemical (activity) and different combination of molecular descriptors. The essential target is to derive a significant and useful equation which could explain the corrosion efficiency of a compound that depends on physical and chemical properties of the molecules [13]. Therefore this approach can be applied to any area and predict certain activity of interest apart from corrosion inhibition performance.

However, different quantum chemical approach and Quantum chemical calculation have been reported as a promising method used to evaluate the corrosion inhibition activity of the inhibitor in which structure and electronic properties are obtained from the use of computational methodologies by quantum chemical calculations [2].

The aim of this paper is to use QSAR model and predict the corrosion inhibition activity of 2-cylohexylthiophene as potential corrosion inhibitors and to perform quantum chemical calculation based on quantum chemical parameters of the inhibitor compound.

2.0 Computational Details

2.1 QSAR

QSAR model was developed and used to predict the corrosion inhibition efficiency of 2-cyclohexylthiophene. The molecules were drawn in 2D with ChemDraw Ultra version 8, and the structure is converted to 3D by chem3D Ultra 08 and optimized using AM1 with MOPAC. Dragon software version 6.0 [14], was used to calculate the descriptors of the compound. Statistical analysis was performed using Matlab Version 6 to obtain the model. The details of this method is described elsewhere [15].

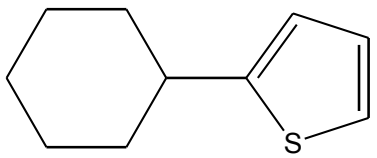

Figure 1. 2-cyclohexylthiophene

2.2 Quantum chemical calculations

Quantum chemical calculations and geometrical optimization of the compound (2-cyclohexylthiophene) were conducted using Density Functional Theory (DFT) with Beeck's Three Parameters (B3) and Lee Yang-Parr (BYP) as (B3LYP) [16,17], (B3LYP) with 6-311G++(d,p) basis set implemented on Gaussian09

program package version 09. Following the geometry optimization different quantum chemical parameters were calculated for the optimized structure such as E_{HUMO}, E_{LUMO}, ΔE_{gap}, Hardness (η), softness (S), dipole moment (μ), electronegativity (X), electron affinity (A), ionization energy (I) and total energy (TE).

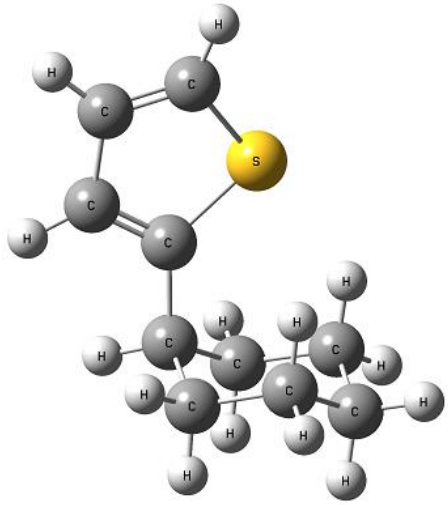

Figure 2. Optimised molecular structure using B3LYP with 6-311++(d,p)

3.0 Results and Discussion

QSAR model correlates the structure and properties of 2-cyclohexylthiophene as corrosion inhibitors, the model recognised to most important descriptors which explained the behaviour of the compound as corrosion potential. The Moran autocorrelation of lag4 weighted by mass (MATS4M) explained the linearity and branching of the compounds while Largest eigen values n3 of Burden matrix weighted by mass (SPMAX3-Bh(m)) shows the role of the nature and size of the neighboring atoms, are the properties responsible for the corrosion inhibition of the compounds. With SPMAX3Bh(m) as the most effective descriptor, with bo, b_1 and b_2 are the regression model constant and coffiecient for descriptor 1 and 2 respectivelyl as shown in Table1. and equation 1

$$\%IE = bo + b_1(MATS4M) + b_2(SPMAX3\text{-}Bh(m)) \quad 1.$$

Table 1. QSAR Model prediction of corrosion inhibition efficiency of 2-cyclohexylthiophee

Compound	bo	b1	b2	MATS4M	SPMAX3-Bh(m	%IE
CHT	-88.25	-9.88	57.27	-0.047	2.87	76.5

Computational chemistry is the approach, which involves quantum chemical calculation and molecular modeling. QSAR approach, was used to obtain many information based on molecular properties of the compounds. However, geometry of the inhibitors and the nature or behaviour of frontier orbital i.e. HOMO and LUMO were among the most significant properties related to inhibition effect. Therefore the inhibiting effect of 2-cyclohexylthiophene was investigated by quantum chemical calculation using Quantum chemical parameters. The optimized structure of the compound and frontier orbital are shown in Figure 2 and quantum chemical parameters calculated are shown in Table 2. Frontier orbital are reported to be responsible for adsorption of the inhibitor on to the metal surface [18,13,19]. Therefore, HOMO energy value of the inhibitor, -6.259eV, as shown in Table 2, makes the inhibitor to have greater tendency to offer electron to the empty d-orbital's of the metals surface and lead to higher corrosion inhibition efficiency of 2-cyclohexylthiophene. LUMO energy was found to be 0.490 eV which make the inhibitor easier to accept electron from the metal atom. More over the energy gap, $\Delta E_{gap} = E_{LUMO} - E_{HUMO}$, was calculated to be 5.769eV which gives better adsorption and increases the reactivity and at the same time lower the energy to remove electron from the unoccupied molecular orbital. It has been reported that lower energy gives better adsorption with the metal surface and hence higher inhibition efficiency and stability [20-22,13]. Dipole moment (μ) of the compound was found to be 0.915 debye which shows an improvement of the adsorption of

the inhibitor to the metal surface, as the higher μ value increases the adsorption of the inhibitor to the metal surface [23]. Softness and hardness are the properties which measured the stability and reactivity of the molecule. Softness of the inhibitor describes the ability of atom or group of atoms to receive electrons while the hardness shows the resistance toward deformation or polarization of the electron cloud of an atom or group of atoms. Therefore, simple electron transfer is usually taken place at the part of the molecules where there is higher value of softness hence higher inhibition efficiency [24-26]. The softness of the inhibitor (S) was found to be 123.236 eV and the hardness η = 6.259eV. According to the Kopman theorem [27], the electroaffinity (A) and ionization energy can be calculated from the HOMO and LUMO energy values. I = $-E_{HUMO}$, A= $-E_{LUMO}$ and the value of electronegativity (X), hardness (η), Softness (S) are calculated using values of I and A. $X = \frac{I+A}{2}$, $\eta = \frac{I-A}{2}$ and $S = \frac{1}{\eta} = \frac{2}{I-A}$ and the values are shown in Table 2.

Table 2. Quantum chemical parameters calculated using B3LYP/6-311G++(d,p)

Quantum chemical parameters	Values
E_{HUMO} / eV	-6.259
E_{LUMO} / eV	-0.490
ΔEgap eV	5.769
Dipole Moment (Debye)	0.915
Hardness (η) eV	6.014
Softness eV	123.266
Ionization energy(I) eV	6.259
Electron affinity(A) eV	0.490
Electronegativity (X) eV	3.320
Total energy (TE) Ev	-21436.826

Previous work reported that values of quantum chemical parameters explained the inhibition effect as a result of electron donation to the metal surface [23,12,22]. Therefore, cycloakyl in 2CHT molecule is an electron donor while mild steel is the electron acceptor, thus forming adsorption inhibition layer against corrosion. This could best be explained by the presences of N or S or O in an organic compound with one pole is adsorbed on to metal surface forming a complex layer bonding to the metal surface polar bonds. Steric hindrance, geometry of the compound, also may explain how the adsorption performance and corrosion inhibition efficiency might be [28].

Therefore, the presence of sulphur atom, lone pair of electron and delocalized π-electron as well as the donor group (cycloalkyl) make the electronic density of 2-cyclohexylthiophene to increase and hence increases adsorption on metal with good corrosion inhibition efficiency.

4.0 CONCLUSIONS

Computational chemistry calculation shows that corrosion inhibition efficiency can be predicted using QSAR as a detecting tool before running the experimental evolution. In addition, calculated quantum chemical parameters such as E_{HUMO}, E_{LUMO}, ΔEgap, dipole moment (μ), softness (S), hardness (η), electonegativity (χ), electron affinity (A), ionization energy (I) and total energy (TE) were efficiently suggested that 3cyclohexylthiophene is a good potential corrosion inhibitor. This conclusion was supported by the prediction of the QSAR model based on the molecular descriptors as Moran autocorrelation of lag4 weighted by mass (MATS4M) which explain the linearity and branching of the compounds and largest eigen values n3 of Burden matrix weighted by mass (SPMAX3-Bh(m)) which describes the nature and size of the neighboring atom.

ACKNOWLEDGEMENT

The authors thanks computational chemistry laboratory and Research Management Centre (RMC), Universiti Teknologi Malaysia. Also acknowledge the support given by Bayero University, Kano. Nigeria and McArthur Research grant to undertaken. PhD program at Universiti Teknologi, Malaysia.

REFERENCES

[1] El Ashry, E. S. H., El Nemr, A. Esawy, S. A. and Ragab, S. (2006) "Corrosion inhibitors Part II: Quantum Chemical Studies on the Corrosion Inhibitors of Steel in Acidic Medium by Some Triazole, Oxadiazole, Triazole and Thiadiazole Derivatives " *Electrochimica Acta*, 51, 19, 3957–3968.

[2] Zarrouk, A., Dafali, A., Hammouti, B., Zarrok, H., Boukhris, S., and Zertoubi, M.,(2010) "Synthesis , Characterization and Comparative Study of Functionalized Quinoxaline Derivatives towards Corrosion of Copper in Nitric Acid Medium, *Int. J. Electrochem. sci*. 5, 46–55.

[3] Rani B. E. A and Basu, B. B. J. (2012). "Green Inhibitors for Corrosion Protection of Metals and Alloys: An Overview," *International Journal of Corrosion*, 2012, i,1–15.

[4] Zarrouk, A., Hammouti, B., Dafali, A., Bouachrine, M., Zarrok, H., Boukhris,S., and Al-Deyab, S.S. (2011). "A theoretical study on the inhibition efficiencies of some quinoxalines as corrosion inhibitors of copper in nitric acid," *Journal of Saudi Chemical Society*, in press.

[5] Masoud, M. S., Awad, M. K., Shaker, M. A. and El-Tahawy, M. M. T. (2010). "The role of structural chemistry in the inhibitive performance of some aminopyrimidines on the corrosion of steel," *Corrosion Science*, 52, 7,2387–2396.

[6] Awad, V. M., Mustafa, R.and Elnga, M. M. A. (2010). "Computational simulation of the molecular structure of some triazoles as inhibitors for the corrosion of metal surface," *Journal of Molecular Structure: THEOCHEM*, 959, 1–3,66–74.

[7] Mert, B. D., Erman M., Mert, Kardaş, G. and Yazıcı, B. (2011). "Experimental and theoretical investigation of 3-amino-1,2,4-triazole-5-thiol as a corrosion inhibitor for carbon steel in HCl medium," *Corrosion Science*, 53,12,4265–4272.

[8] . Döner, A., Solmaz, R., Özcan, M., and Kardaş, G. (2011). "Experimental and theoretical studies of thiazoles as corrosion inhibitors for mild steel in sulphuric acid solution," *Corrosion Science*, 53, 9, 2902–2913.

[9] Halambek, J., Jukić, M., Berković, K., and Vorkapić-furač, J. (2012) "Investigation of Novel Heterocyclic Compounds as Inhibitors of Al-3Mg Alloy Corrosion in Hydrochloric Acid Solutions," *Synthesis*,7. 1580–1601.

[10] Khaled, K. F., (2012). "Understanding Corrosion Inhibition of iron by 2-Thiophenecarboxylic Acid Methyl Ester : Electrochemical and Computational study," *Adsorption Journal Of The International Adsorption Society*, 7,1027–1044.

[11] Olivares-xometl, O., Likhanova, N. V., Nava, N., and Prieto, A.C. (2013). "Thiadiazoles as Corrosion Inhibitors for Carbon Steel in H 2 SO 4 Solutions," *Test*, vol. 8, 735–752.

[12] El Ashry, E. S. H., AEl Nemr, A. and Ragab, S. (2012) "Quantitative structure activity relationships of some pyridine derivatives as corrosion inhibitors of steel in acidic medium.," *Journal of molecular modeling*, vol. 18, 3,1173–88.

[13] Khaled, K. F. (2011) "Modeling corrosion inhibition of iron in acid medium by genetic function approximation method: A QSAR model," *Corrosion Science*, 53,11, 3457–3465.

[14] Todocheni. R. (2009)"Author ' s personal copy, 4, 129–172.

[15] Usman, B., Maarof., Abdallah, H. H., Jamaludin, R. and Al-fakih, A. M., Aziz, M. (2014). "Corrosion Inhibition Efficiency of Thiophene Derivatives on Mild Steel : A QSAR Model .," *Int. J. Electrochem. sci* , 9, 1678–1689.

[16] Lee, C., Yang, W. and Parr G.R.(1988)." Developmenet of the Collec-Salvetti correlation energy formula into a fundemental of the electron density" , *Physical Review* 27, 7.

[17] Becke, A. D (1993). " Density -Functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys*, 9, 7.

[18] Zarrok, H., Oudda, H. Zarrouk, A., Salghi., Hammouti, B., and Bouachrine, M., (2011). "Weight Loss Measurement and Theoretical Study of New Pyridazine Compound as Corrosion Inhibitor for C38 Steel in Hydrochloric Acid Solution," *Methods*, 3, 6, 576–590, 2011.

[19] Wang, Y. Jing, H., Mehta, V., Welter, G. J. and Giammar, D. E. (2012)"Impact of galvanic corrosion on lead release from aged lead service lines," *WR*, 46, 16, 5049–5060.

[20] Bereket, G., and Hu, E., (2002). "Quantum chemical studies on some imidazole derivatives as corrosion inhibitors for iron in acidic medium," *Journal of Molecular Structure*, 578, 2002.

[21] Bentiss, F., Lebrini, M. and Lagrenée, M. (2005). "Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system," *Corrosion Science*, 47, 12, 2915–2931, 2005.

[22] Gece, G. and Bilgiç, S.(2010) "A theoretical study on the inhibition efficiencies of some amino acids as corrosion inhibitors of nickel," *Corrosion Science*, 52, 10, 3435–3443.

[23] Zarrouk, A., Zarrok, H., Salghi, R., Hammouti, B., Touzani, R., and. Bouachrine, M. (2012). "A Theoretical Investigation on the Corrosion Inhibition of Copper by Quinoxaline Derivatives in Nitric Acid Solution," *Int. J. Electrochem. sci,* 7, 6353–6364.

[24] Obot I. B. and Obi-Egbedi, N. O (2010) "Theoretical study of benzimidazole and its derivatives and their potential activity as corrosion inhibitors," *Corrosion Science*, 52, 2, 657–660.

[25] Obot, I. B., Umoren, S.A. and Ebenso, E.E.(2011). "Computational Simulation and Statistical Analysis on the Relationship Between Corrosion Inhibition Efficiency and Molecular Structure of Some Phenanthroline Derivatives on Mild Steel Surface," *Quantum*, 6, 5649–5675.

[26] Eddy, N. O., Awe, F. E., Gimba, C. E., Ibisi, N. O., and Ebenso, E. E. (2011) "QSAR , Experimental and Computational Chemistry Simulation

Studies on the Inhibition Potentials of Some Amino Acids for the Corrosion of Mild Steel in 0 . 1 M HCl," *Most*, 6, 931–957.

[27] Torrent-Sucarrat, M., De Proft, F., Ayers, P.W and Geerlings, P., (2010)"On the applicability of local softness and hardness.," *Physical chemistry chemical physics : PCCP*, 12, 5,1072–80.

[28] Fouda A. S. and Wahed, H. A. A. (2011) "Corrosion inhibition of copper in HNO3 solution using thiophene and its derivatives," *Arabian Journal of Chemistry*, *In Press*.