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Short Communication

Computational Evaluation of the Effect of Structural Parameters of 3-Flouro Thiophene and 3-thiophene Malonic Acid on Corrosion Inhibition Efficiency of Mild Steel in Acidic Media

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The effect of the substituent's, halide and carboxylic group on thiophene compounds, namely 3-flourothiophene (3FT) and 3-thiophene malonic acid (3TMA) on the corrosion inhibition efficiency of mild steel in acidic media has been predicted using quantitative structure activity relationship (QSAR) model and quantum chemical calculation. The results from QSAR model show that 3TMA exhibit higher corrosion inhibition efficiency of 85.3 and 91.7%, which may be due to the increase in length of the malonic acid then 3FT which tends to exhibit higher electron withdrawing ability as a result of the fluorine substitution and hence lower corrosion inhibition efficiency of 40.6 and 42.1% respectively. Similarly the molecular structure of the compounds was investigated using density functional theory (DFT) calculation with 6-311G++(d,p) basis set. Quantum chemical parameters were calculated, the results show that QSAR model can be used to predict the corrosion inhibition performance of a compound prior to experimental.

Keywords: Corrosion Inhibition, QSAR, 3-Flourothiophene, 3-Thiophene Malonic acid, DFT

1. INTRODUCTION

The use of metal such as mild steel in industrial and household application is very significant [1-3]. Mild steel is found to have low corrosion resistance hence need to be protected against corrosion

[1]. Materials that are used for the removal of rust are acid solution such as hydrochloric acid and sulphuric acid, which are widely used in industrial application such as acid pickling, washing, acid cleaning and oil refining and cleaning [4].

The use of organic inhibitors to handle this problem were found to be the best alternative method in industrial and other applications [5,6]. Many inhibitors have been reported to be used as good corrosion inhibitors [7-9]. One of the specific difficulties is the choice of the inhibitors as a result of different types of corrosion system. Organic inhibitors containing N, S and O atom are well known corrosion inhibitors. They have the ability to form stronger coordination bond with metal atoms. The inhibition efficiency is in the order of O < N < S [5,10]. In addition, organic inhibitors containing more than one active atom (N and O for example) exhibit better performances in inhibition than those containing N or O atom [11,12].

In this work the effect of the molecular structure of 3-fluoro thiophene and 3-thiophene malonic acid as corrosion inhibitors have been predicted using QSAR model developed from molecular descriptors obtained from Dragon software. The performances of the inhibitors are then evaluated by quantum chemical calculation through the production of physical and chemical descriptors to support the QSAR model.

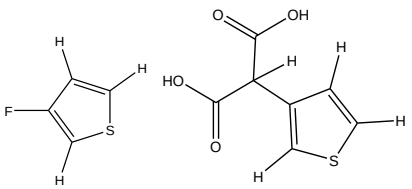
2. COMPUTATIONAL DETAILS

2.1 QSAR Model

QSAR model has been developed and was used to predict the corrosion inhibition efficiency 3-flouro thiophene and 3-thiophene malonic acid acid. The molecules were optimized using Austin model 1 (AM1) with molecular orbital package (MOPAC). Dragon software version 6.0 [13] was used to calculate the molecular descriptors while the statistical analysis was carried out by matlab version 7.9 as described elsewhere [14,15].

2.2 Quantum chemical calculation details

Quantum chemical calculations were carried out using Gaussian 09 program [16,17]. Complete geometry optimization of the molecules were carried out by B3LYP at the 6-311G++(d,p) basis set [18,19]. DFT has been recognized as an accurate method for evaluating the performance of inhibitors characteristics and corrosion inhibition mechanism based on structural properties of the inhibitors in corrosion process [20]. Molecular structure and names of the inhibitors are presented in Figure 1.



(a) (b)

Figure 1. Molecular structure of (a) 3-flourothiophene and (b) 3-thiophene malonic acid

3. RESULTS AND DISCUSSION

3.1 QSAR model

Quantitative structure activity model was built using descriptors calculated from Dragon software presented in Table 1. Descriptors with positive values represent higher contribution and higher activity. RDF010S descriptor has shown significant contribution in the activity 3TMA and 3FT with values 14.05 and 2.702 respectively. Similarly, the lowest contribution is found for MATS4M with 0.213 and 0.497 respectively. Two models are shown using equations 1 and 2. Model 1 is represented by 5 descriptors while model 2 is represented with 2 descriptors namely Moran autocorrelation of lag4 weighted by Mass (MATS4M) and spectral absolute deviation from Laplace (SpMax-Bh3(m)) .

Table 1. Molecular descriptors and their values

Compounds	Molecular descriptors				
	SpMad_L	MATS4M	SpMax3_Bh(m)	RDF010S	R1p
3-Flourothiophene	1.307	0.497	2.362	2.702	0.735
3-Thiophene melonic acid	1.454	0.213	3.067	14.025	0.926

The generated models obtained were presented by equation 1 and 2.

%IE=135.541+[8.4374(SpMad_L)]+[6.8488(MATS4M)]+68.467(SpMax3-Bh(m))+ [- 0.497 (RDF010S)] + 41.111(RiP) (1)

R^2 =0.9920, R^2_{cv} = 0.5854, R^2_{pre} = 0.5999, RMSEC= 1.148 N= 11

%IE = -88.246 + [-9.881 (MATS4M)]+57.272 (SpMax3-Bh(m)) (2)

R^2 =0. 9295, R^2_{cv} = 0.8481, R^2_{pre} = 0.5114, RMSEC= 3.145, N= 11

The models were used to calculate the inhibition efficiency of the compound and the results show that 3TMA exhibit higher inhibition efficiency due to the presence of steric hindrance and additional functional groups as well as the pi –electron in the thiophene rings which enhance the electron donation ability to the empty d-orbital of the metal atom and lead to higher IE [21,22]. Flouro group as a higher electron withdrawing group tends to have lower tendency to release electron to the metal atom which contribute to lower inhibition efficiency as shown in Table 2.

Table 2. The predictive ability of the models for the proposed compound

Compounds	%IE compound predicted	
	A(5 descriptors)	B (2 descriptors)
3-Flourothiophene	40.6	42.1
3-Thiophene malonic acid	91.7	85.3

3.2 Quantum chemical calculation

Two thiophene compounds have been studied namely, 3-Flourothiophene (3FT) and 3-Thiophene Malonic Acid (3TMA),. The derivatives are chosen to show the effect of molecular structure and molecular electronic properties based on the nature of substituent.

The study was carried out by calculating the quantum chemical parameters of set of compounds presented in Figure 2. From the QSAR model, 3TMA exhibits higher corrosion inhibition with 85.3 and 91.7 % while 3FT shows 40.6 and 42.1% respectively.

Quantum chemical calculations using DFT at 6-311G++(d,p) basis set were carried out in this part of the work on 3FT and 3TMA thiophene compounds to evaluate the performance of the studied compounds as corrosion inhibitors. The optimized structures are presented in Figure 2.

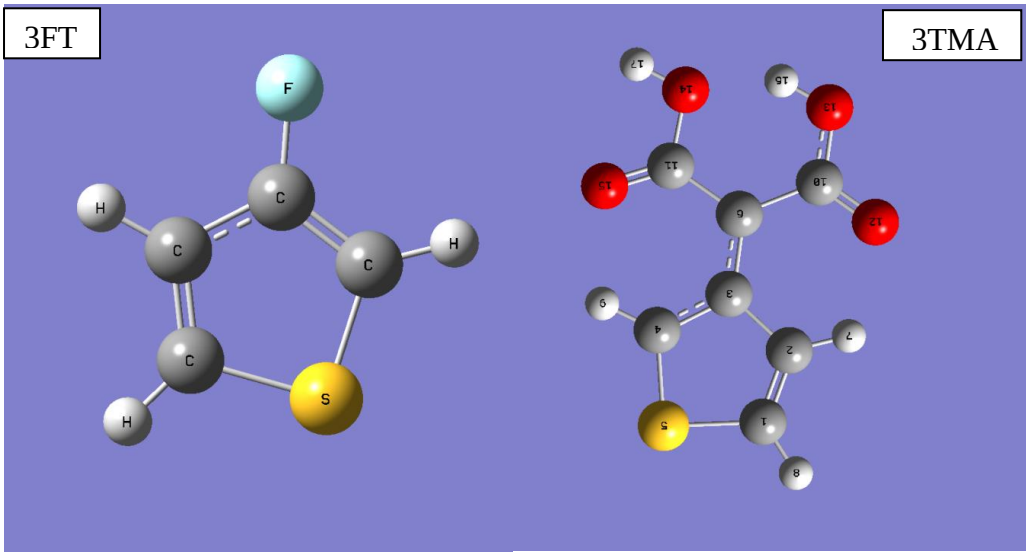


Figure 2. Optimized structures of 3-flourothiophene and 3-thiophene malonic acid

The values of the calculated quantum chemical parameters such as the energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (E_{LUMO}-E_{HOMO})= ΔE_{gap} and dipole moment (μ), are presented in Table 3.

Table 3. Quantum chemical descriptors calculated using B3LYP/6-311G++ (d,p) thiophene derivatives

Compounds	Quantum chemical parameters			
	$E_{HOMO\ (au)}$	$E_{LUMO\ (au)}$	ΔEgap (au)	Dipole Moment (Debye)
3-flouro thiophene	-0.2612	-0.059	0.203	1.435
3-thiophenemelonic acid	-0.245	-0.150	0.095	3.367

The interactions between the inhibitor molecule with mild steel surface have been observed according to the influence of energy of HOMO, LUMO, ΔE_{gap} and dipole moment [23].

Other important quantum chemical parameters used in this study are electronegativity (X), electron affinity (A), softness (S), ionization energy (I), hardness (η), and total energy (TE) are presented in Table 4.

Table 4. Quantum chemical descriptors calculated using B3LYP/6-311G++ (d,p) thiophene derivatives

Compounds	Quantum chemical parameters					
	X, (au)	η, (au)	S, (au)	I (au)	A (au)	TE(au)
3-flouro thiophene	0.189	0.232	4.304	0.262	0.059	-652.3
3-thiophene melonic acid	0.273	0.170	5.875	0.245	0.150	-969.0

Comparing the results obtained from the quantum chemical calculation in Tables 3 and 4, with QSAR model in Table 2, shows that the predicted %IE by QSAR is consistent with the quantum chemical calculations. E_{HUMO} is associated with electron donating ability of the molecule. The higher the value of E_{HUMO}, the higher tendency of the molecule to release the electron to the empty orbital of the metal surface [24,25]. Therefore, 3TMA with E_{HOMO} (-0.245au) is higher than E_{HOMO} of 3FT (-0.262), as shown in Tables 3 and 4, hence higher inhibition efficiency for 3TMA. Similarly, lower value of E_{LUMO} indicated higher possibility to accept electron by the acceptor [26]. The result show that 3TMA has lower E_{LUMO} of (-0.150au) while 3FT having (-0.058).

Energy gap (ΔE_{gap} =E_{LUMO}-E_{HOMO}) is one of the important parameters in quantum chemical calculations that considered as a function of reactivity of the inhibitor molecule towards adsorption on to the metal surface. Lower value of ΔE_{gap} gives higher reactivity and inhibition efficiency of the inhibitor compounds [25]. Therefore, ΔE_{gap} value of 3TMA and 3FT are 0.095au and 0.203au respectively. The value of dipole moment (μ) was observed to be higher in 3TMA as 3.367 debye while for 3FT the μ value is 1.435 debye. It has been reported that higher value of dipole moment increases measurements of the polarity in the covalent bond which increases the adsorption between the inhibitor and the metal surface [27]. Therefore, lower E_{gap} and higher μ values in 3TMA indicated higher reactivity to accept the electron and formed a strong dipole –dipole interaction between the metal surfaces than 3FT.

The values of the other calculated quantum chemical parameters such as ionization energy (I), electron affinity (A), hardness (η), softness (S) are obtained using Koopman's theory [28], are presented in Table 4. According to Hartree -fork theory, the frontier orbital was calculated from the relationship I= -E_{LUMO}, A= -E_{HOMO}, $\eta = \frac{I-A}{2}$, $S = \frac{1}{\eta} = \frac{2}{I-A}$ From the results observed in Table 3, electronegativity value for TMA is (0.273au) which is higher than that of 3FT (0.237au), and the hardness value of 3TMA (0.170au), is lower than that of 3FT(0.232au) while S found to be higher in 3TMA (5.878au) with 3FT having S (4.302au) . Therefore, from the results in Table 4, the properties

explained the ability of the molecule to release electrons to the metal surface. Reactivity and stability of the molecules is explained by lower value of η and higher value S from the results 3TMA is expected to exhibit higher inhibition efficiency.

The value of ionization energy (I) and electron affinity (A) were also calculated and the 3TMA results show lower value of ionization energy , (0.245au) and higher value of electron affinity (0.150au) while 3FT has the values (0.262au) and (0.0519au) of I and A respectively. Higher tendency to donate and accept the electron is expected to be higher in 3TMA than 3FT. The total energy value of the inhibitor indicates the stability of the compound and the influence of the electron density. Lower energy gives better stability and higher efficiency for corrosion inhibition to the metal surface [29]. The results in Table 3 show that 3TMA exhibits higher inhibition efficiency and stability with the TE value of (-969.0au) while 3FT has TE value of (-652.3au) which has lower inhibition efficiency and lower stability than 3TMA.

4. CONCLUSION

The effect of the structure of 3TMA and 3FT on the corrosion inhibition performance on mild steel surface was predicted using QSAR model. The performance was evaluated and supported by quantum chemical calculation using quantum chemical parameters. Comparative correlations of these inhibitors revealed that the inhibition efficiency predicted is consistence with quantum chemical evaluation with 3TMA having higher performance in corrosion inhibition than 3FT. This is attributed to the molecular structure and the electronic properties of the compounds as a function of their activity. In addition new descriptors were found to be associated with the evaluation of corrosion performance using dragon software namely MATS4M which explain the effect of size and nature of neighboring atoms as well as SpMax3_Bh (m) which explain the linearity and branching of the compound as the most important structural properties to define the ability of the compound to inhibit corrosion.

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