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THEORETICAL AND EXPERIMENTAL STUDIES OF CORROSION INHIBITION OF THIOHENE-2-ETHYLAMINE ON MILD STEEL IN ACID MEDIA

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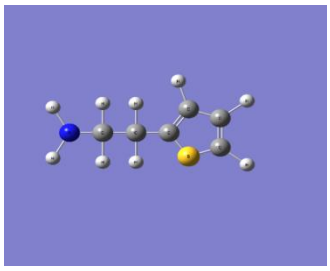
Graphical abstract



Abstract

Corrosion inhibition of mild steel in 0.5M H_2SO_4 at 30°C with thiophene-2- ethylamine (TEA) as inhibitor has been assess by quantitative structure activity relation (QSAR) model and quantum chemical calculations. The results were evaluated using weight loss and electrochemical methods such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). The results showed good performance of TEA in corrosion protection which behaves as mixed inhibitor from PDP. The micrograph from FESEM and EDX dot mapping showed that the inhibitor adsorbed onto the metal surface with different distribution for S, C and N atoms which indicate less damage on the metal surface in the presence of TEA.

Keywords: Corrosion inhibitor, QSAR, quantum chemical calculation, electrochemical methods, Thiophene -2-ethylamine

Abstrak

Perencatan kakisan keluli lembut dalam 0.5M H_2SO_4 pada 30°C dengan thiofena-2-etilamina (TEA) sebagai perencat telah dinilai dengan model kuantitatif berhubung aktiviti struktur (QSAR) dan pengiraan kimia kuantum. Keputusan telah dinilai menggunakan kaedah kehilangan berat dan kaedah elektrokimia seperti polarisasi potentiodinamik (PDP) dan spektroskopi impedans elektrokimia (EIS). Hasil kajian menunjukkan prestasi baik TEA dalam perlindungan kakisan yang berkelakuan sebagai perencat percampuran PDP. Mikrograf dari FESEM dan EDX pemetaan dot menunjukkan bahawa perencat terserap ke dalam permukaan logam dengan pengagihan berbeza untuk atom S, C dan N yang menunjukkan kerosakan yang kurang pada permukaan logam dengan kehadiran TEA..

Kata kunci: Perencat kakisan, QSAR, pengiraan kuantum kimia, kaedah elektrokimia, Thiofena-2-etilamina

1.0 INTRODUCTION

Corrosion protection processes for mild steel in acidic media are found to be significance [1]. The industrial application of acid for example sulphuric acid and hydrochloric acid in acid pickling, industrial cleaning, descaling and acidization of wells are found to be efficient and economically favorable [2]. The most common method for corrosion control is the use of chemical for corrosion inhibition [3, 4]. Heterocyclic compounds containing O, N, S and P have attracted many researchers and proved to be good in corrosion protection [5]. Today, the study of thiophene and its derivatives as corrosion inhibitors is a good area of research [6]. This is due to the nature of their molecular structure, which contain S and the aromaticity is closer to that of benzene, hence has tendency to donate electron which give good corrosion inhibition efficiency.

Computational method have been used and proved to be powerful tool for studying the relationship between molecular structure and corrosion inhibition performance of molecular compound [7]. However, quantitative structure activity relationship (QSAR) and Quantum chemical calculation are found to be good methods in predicting the correlation between molecular structure and corrosion inhibition on metal surfaces prior to experimental evaluation [8, 5].

Thiophene -2- ethylamine (TEA) is a thiophene based compound with molecular structure containing N and S atoms with pi-electron which have higher tendency to donate electron to the empty d-orbital of the metal atom. The aims of this study are to predict the corrosion inhibition performance of TEA on mild steel in acidic media using QSAR and to evaluate the predicted results with quantum chemical calculations, electrochemical methods and surfaceanalysis using FESEM, EDX and optical microscope. The structure of TEA is presented in Figure 1.

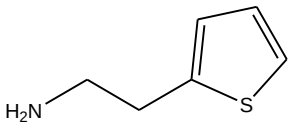


Figure 1 Molecular structure of thiophene-2-ethylamine

2.0 EXPERIMENTAL

2.1 QSAR

QSAR model was generated and used to predict the corrosion inhibition efficiency of thiophene-2-ethylamine. The molecular structure were generated and standardized by optimization using Austin Model one (AM1), with molecular orbital Package (MOPAC). Dragon software version 6.0 was used to generate molecular descriptors and Matlab version 7.9 for statistical analysis as described elsewhere [9].

2.2 Quantum Chemical Calculations

Quantum chemical calculations were carried out using Gaussian09 software. Density functional theory (DFT) [3], was used to calculate and obtain the quantum chemical descriptors. The optimization of the molecules was performed using DFT at Becke three Yarg and Parr with 6-311G++(d,p) basis set as B3LYP/6-311G++(d,p) [4, 5].

2.3 Electrochemical Method

The potentiodynamic polarization measurements were carried out using three electrodes namely working electrode (WE), reference electrode (RE) and counter electrode (CE). Polarization measurements were carried out using Autolab PGSTAT 30 model and VerstaSTAT 3.50 model in computer control, the analysis were carried using GPES and FRA.

2.4 Potentiodynamic Polarization

Before the polarization the mild steel sample was prepared with the dimension of (2 cm x 2 cm x 2 mm). The sample was ground and polished with emery paper of grade 240, 400, 800 and 1000 respectively and washed with distilled water followed by acetone and dried with air and kept in desiccators before application. The polarization parameters used are scan rate of $5mVs^{-1}$ with the potentiostart range of ±250mV at open circuit current (OPC) with steady time of 15 minutes. The inhibition efficiency at a given concentration was calculated using Equation 1, [10].

$$\%IE = \frac{I_o - I}{I_o} \times 100 \quad (1)$$

Where I_o and I are the current density with and without TEA.

2.5 Electrochemical Impedance Measurements

Electrochemical impedance measurements were also carried out using VerstaSTAT 3.47 at open circuit potential (E_{ocp}) of 10 mV over a frequency range of 100kHZ -10Hz peak to peak and the %IE was obtained using Equation 2. The amplitude was measured at 30s with temperature of 30°C. The impedance data were analyzed and obtained the fitted circuit using ZsimpWim 3.10 program.

$$\%\ IE = \frac{R_{ct} - R}{R_{ct}} \times 100 \quad (2)$$

Where R_{ct} and R are charge transfer without and with inhibitor

2.6 Weight Loss

Weight loss measurements were performed in a 250 mL beaker at 30°C. The solution volume used is 250 mL and the mild steel was weighed and immersed in the solution for 1 hr after the mild steel sample was

retrieved and washed with distilled water and rinsed with ethanol and acetone and dried and reweighed and the %IE was obtained using Equation 4.

$$\theta = \frac{W_{un} - W_{in}}{W_{un}} \quad (3)$$

$$\%IE = \frac{W_{un} - W_{in}}{W_{un}} X\ 100 \quad (4)$$

3.0 RESULTS AND DISCUSSION

The molecular descriptor generated for QSAR model building are presented in Table 1. Considering the QSAR model predictive ability and the number of descriptor. A good model was obtained for TEA using partial least square analysis given in Equation 5 and 6 [9].

%IE = -135.541 + [-8.4374(SpMad_L)] + [6.8488(MATS4M)] + 68.467(SpMax3-Bh(m)) + [-0.497(RDF010S)] + 41.111(RiP) (5)

R^2 =0.9920, R^2_{cv} = 0.5724, R^2_{pre} = 0.5999, N=11

%IE = -88.246 + [-9.881 (MATS4M)] + 57.272 (SpMax3-Bh(m) (6)

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

Where R^2 is the regression coefficient, R^2_{cv} is the regression coefficient of cross validation and R^2_{pre} is the regression coefficient of prediction and RMSEC is the root mean square error of calibration. The models show significant statistical quality. The selected descriptors in Equation 1 and 2 are presented in Table 1.

Comparing Equation 1 and 2 the values of regression coefficient varies, with Equation 2 has larger value of R^2, R^2_{cv} and RMSEC and lower value of R^2_{pre} which gives good statistical quality. The values of the descriptors presented in Table 1 explain the effect of SpMad_L, MATS4M, SpMax3_Bh(m), RDF010S and R1p descriptors on corrosion inhibition performance of TEA. The descriptors selected in building the model belong to topological, 2D, edge adjancy, 3D and radial molecular descriptors, explained the connectivity of the atom related to chemical bonding, effect of branching, adjancy of the atom in terms of neighboring atom, molecular density and bond formation and polarization respectively.

Therefore, the models were used to predict the corrosion inhibition efficiency of TEA as presented in Table 2. The results indicate higher %IE in the first model as 69.8% with second model having 66.1%, with 5% difference which shows the inhibition efficiency is similar. However, it has been stated that a model with few number of descriptors is considered as the best model [11, 12].

Table 1 Molecular descriptors and their values

Compound and abbreviation		Molecular descriptors				
Compounds		SpMad_L	MATS4M	SpMax3_Bh(m)	RDF010S	R1p
Thiophene-2-ethylamine	TEA	-1.299	-0.072	2.682	11.851	0.926

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

Compounds	%IE compound predicted	
	A	B
Thiophene-2- ethylamine	69.8	66.1

A= Model 1 with 5 descriptors, B = Model 2, with 2 descriptors

3.1 Quantum Chemical Calculation

The optimized geometry of the TEA molecules is shown in Figure 2. The values of the quantum chemical descriptors calculated are presented in Table 3. It can be observed that the values of E_{HUMO}, E_{LUMO}, ΔE_{gap} describe the ability of the compounds to release and accept electron from the metal d-orbital 13], therefore, higher value of E_{HUMO}, with lower value of E_{LUMO} and ΔE_{gap} the better the release and acceptance of electron by TEA, hence the E_{HUMO} (-0.241au), E_{LUMO} (-0.023) and ΔE_{gap} (0.218au) give good inhibition efficiency. According to Koopman's theory [13], electronegativity (X), ionization energy (I), and electron affinity (A) are given as A = $-E_{LUMO}$, I = E_{HUMO} while Electronegativity (X), hardness (η) and softness (S) were given as X= (I+A)/2 , η = (I-A)/2, S = I/η or 2/(I-A).

It has been established that there is no relationship between dipole moment with %IE experimentally [14].

Similarly η and S measured the stability of molecules and hard molecules have higher ΔE_{gap} while soft molecules have smaller ΔE_{gap}, and molecules with lower value of η and higher value of S tend to give good corrosion inhibition efficiency [14]. Lower values of A, I and higher X and TE give better inhibition efficiency [15]. The values of X, I, A, S and η for TEA are given as 0.143, 0.229, 0.023, 4.362, 0.229 and -687.0 au respectively gives chance for TEA to be good corrosion inhibitor.

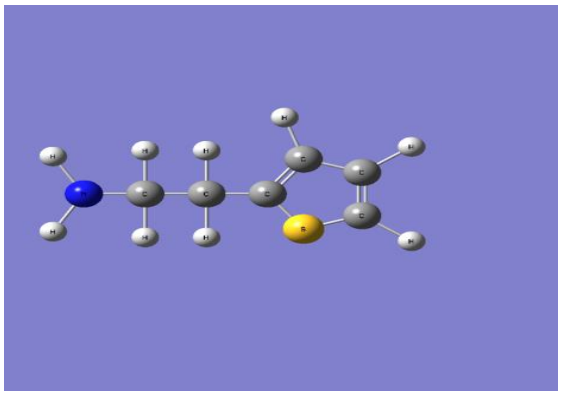


Figure 2 Optimized structure of TEA

Table 3 Values of quantum chemical descriptors

Descript.	HUMO (au)	LUMO (au)	ΔE_{gap}	μ (debye)	X (au)	I (au)	A (au)	S (au)	η (au)	TE (au)
values	-0.241	-0.023	0.218	0.844	0.143	0.229	0.023	4.362	0.229	-687.0

3.2 Electrochemical Methods

The performance of TEA on the electrochemical polarization behavior of mild steel in 0.5M H_2SO_4 has been studied by polarization measurements and the calculated parameters such as I_{corr}, E_{corr}, b_a, b_c and %IE from the Tafel plot as in Figure 3. The results are presented in Table 4. It can be observed that from the results in Table 4 both cathodic and anodic were inhibited after addition of TEA to 0.5 M H_2SO_4 solution from the result it shows that TEA is a mixed inhibitor which fall 0.147 to 0.280 mV/ SCE within when compared to blank. It has been stated that a inhibitor can be considered as anodic or cathodic inhibitor if it falls within 85mV/ SCE compared to blank [16]. Hence TEA gives %IE of 69.8 %, with lower corrosion rate. As presented in Table 4.

Table 4 Polarization data of mild steel in 0.5M H_2SO_4 with and without addition of inhibitor at 303k for substituted thiophene derivatives

Compound	C(M)	E_{corr} /mV	-bc/mV(dec.)	-ba/mV(dec.)	C.R in mm/year	I_{corr} (μA/cm²)	%IE
Blank	0.5	- 453	443	427	9.098	783.3	-
TEA	10^{-2}	- 366	147	280	2.75	236.8	69.8

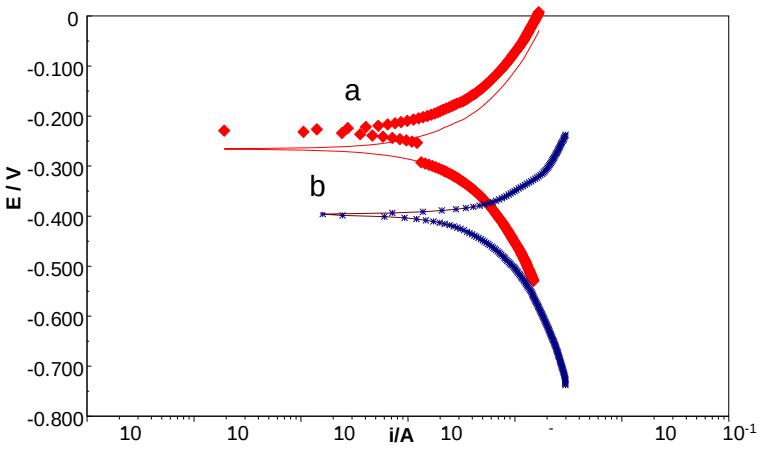


Figure 3 Polarization curves at 30°C in (a) 0.5M H_2SO_4 and(b) Presence of 0.01M TEA

The effect of TEA as corrosion inhibitor in 0.5M H_2SO_4 from Nyquist plot presented in Figure 4a shows a change in the diameter of the semi circle compared to the blank; this is attributed to the addition of the TEA which increases the thickness of the surface due to the formation of a layer on the metal surface. Hence gives higher resistance charge transfer (R_{ct}) which decreases the capacitance double (C_{dl}) [17]. Therefore, bode plot presented in Figure Nyquist plot (4a) and bode plots (4b) and (4c) clearly explained the formation of protective layer on the metal surface due to change in size of the semi circle plots. The percentage inhibition efficiency of TEA is presented in Table 5 the result was calculated using Equation 4.

Table 5 Electrochemical impedance spectroscopy parameters

Compound	R_s (Ω cm²)	R_{ct} (Ω cm²)	C_{dl} x 10^{-5} (μFcm^{-2})	%IE	Equivalent Circuit
Blank	17.6	11.4	7.75	-	R(QR)
TEA	11.8	87.4	4.91	87.0	

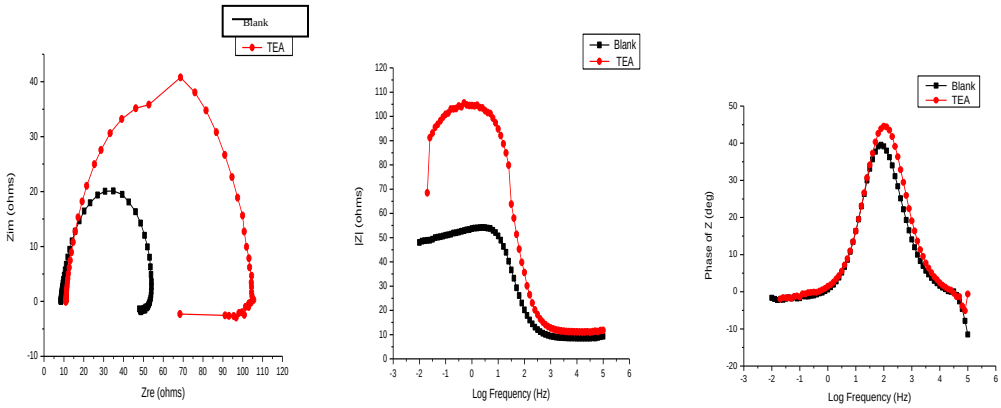


Figure 4 (a) Nyquist plot (b) and (C) bode plot

3.3 Weight Loss

Corrosion rate, surface coverage and %IE for mild steel in 0.5M H_2SO_4 in the absence and presence of 0.01M TEA are presented in Table 6. It can be deduced that the presence of TEA reduced the corrosion rate and with surface coverage of 0.00060 g/cm²hr, this is due to the formation of layer on the metal surface and gives inhibition efficiency of 78.0.% at 30°C as shown in Table 6.

Table 6 The values of inhibition efficiency obtained from the weight loss for mono substituted thiophene derivatives

	Compounds	Weight loss (g)	CR (g/cm²hr)	Θ	%IE
Blank	H_2SO_4	0.011	0.02750	-	-
	TEA	0.0024	0.00060	0.78	78.0

3.4 Surface Analysis

The surface micrograph were analyzed using FESEM, optical microscope and EDX technique to obtain information about the adsorption and formation of layer on the metal surface in the presence and absence of 0.01M TEA as shown in Figure 5-and 6.

The destruction of the metal surface can be observed on Figure 5a and 5c with acid while due addition of TEA the surface of the metal become smooth and less destructive as shown in Figure 5b and 5D.

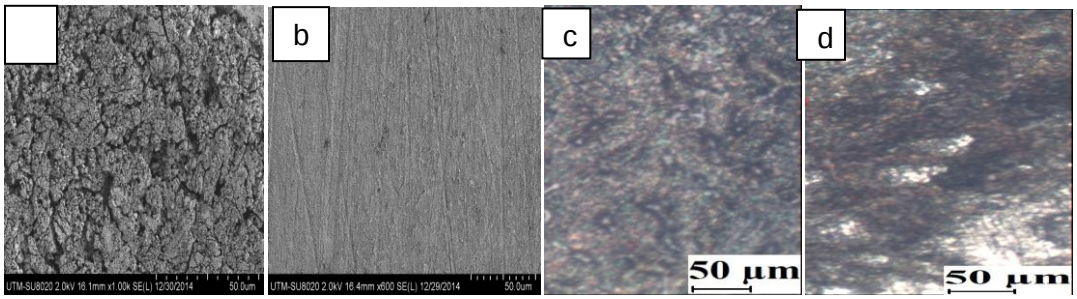
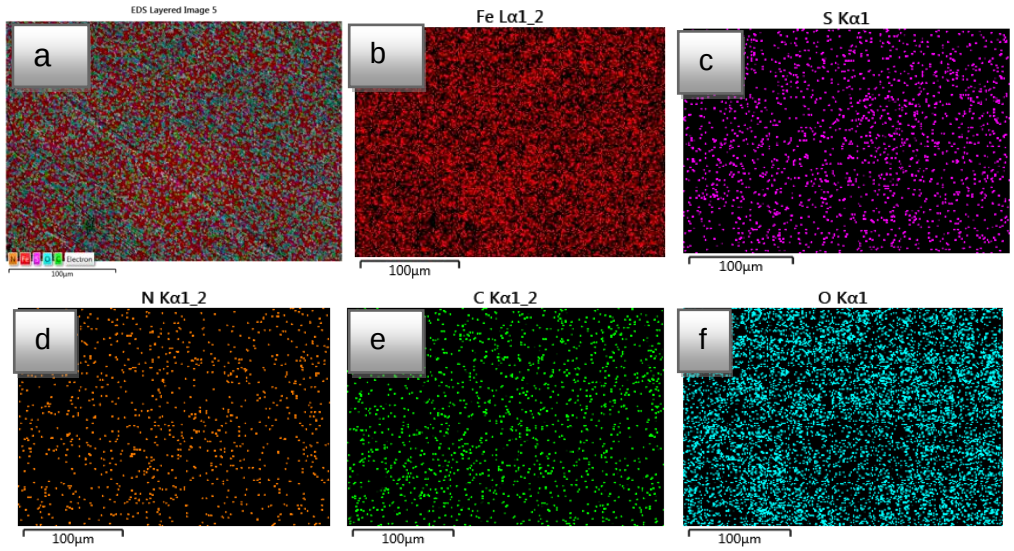


Figure 5 FESEM- and OM micrograph of metal surface atom (a and c) H_2SO_4 (b -C) TEA

The EDX dot mapping was employed to check and study the elemental composition of TEA involved in the inhibition process on metal surface. The distribution of elemental composition of the inhibitor is presented in Figure 6a to g, the EDX spectrum shows the element such S, N, C and O were adsorbed on to metal surface in the presence of TEA.



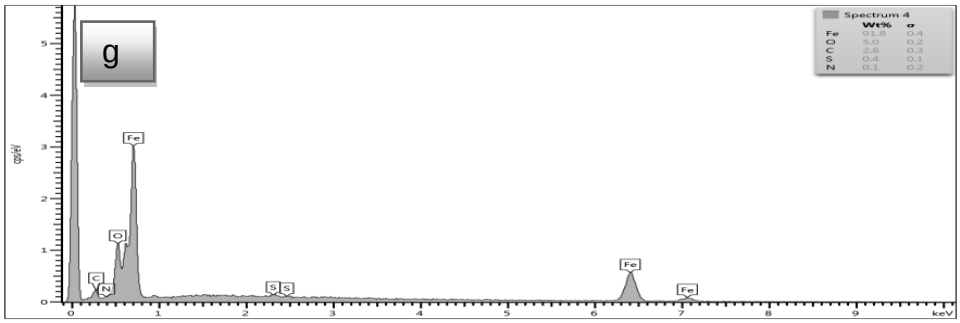


Figure 6 FESEM- EDX dot mapping of TEA solution on metal surface with atom (a) TEA (b) Fe (c) S (d) N (e) C (f) O (g) EDX spectrum of multi-element of containing Fe, S, N, C and O

4.0 CONCLUSION

QSAR model proved to be a good tool for searching new corrosion inhibitors from the molecular structure using new molecular descriptor from dragon software which contain multiple properties.

The results from quantum chemical calculation was found to be consistence with predict result by QSAR model. Potentiodynamic polarization results evaluate TEA as mixed inhibitor and the mechanism of the adsorptions on to the mild steel were explained clearly by EIS as chemical adsorption and all the electrochemical and weight result were found to be consistence with predicted results.

FESEM, optical microscope and EDX proved the existence of corrosion on mild steel in 0.5M H_2SO_4 and the inhibition performance of TEA.

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