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INHIBITION PERFORMANCE OF MILD STEEL CORROSION IN ACIDIC MEDIA USING 2-THIOPHENE ACETYL CHLORIDE

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ABSTRACT

Corrosion inhibition performance of 2-thiophene acetyl chloride (2TAC) in 0.5M $H_2SO_4$for mild steel (MS) was investigated using quantitative structure activity relations (QSAR) model, Potentiodynamic polarization (PDP) and Field emission scanning electron microscopy – energy disperse spectroscopy(FESEM –EDX) dot mapping . The results showed that 2TAC exhibit good corrosion efficiency toward (MS). The inhibitor were adsorbed onto the (MS) surface which block the reaction site for the acid. The performance of the inhibitor were also evaluated using Density Functional Theory (DFT) at B3LYP/ 6-311 G^{++} (d,p) basis set which explain the geometry and quantum chemical parameters and the theoretical data proved that 2TAC is a good inhibitor.

Keywords: Corrosion inhibition, QSAR, DFT, 2-thiophene acetyl chloride

INTRODUCTION

Inhibitors are generally use in corrosion protection for many materials (Arslan et al., 2009). Corrosion of metals particularly mild steel (MS), is a problems of concern that is receiving serious attention (Hmamou et al., 2013). Use of acid solution courses corrosion in industries in order to reduce or stop the corrosion the use inhibitor is found to be the most widely method use for corrosion control. Acid are used in industrial applications such as acid pickling, acid cleaning, acid descaling and oil well descaling. Inhibitors are used to reduce the effect of the attack by acidic media on the metal surface. Many types of organic inhibitor are used to reduce the corrosion attack, the most common inhibitor use are organic compound containing heteroatoms such as N, O, S ,P and those compound with aromatic ring or triple bond, the inhibition efficiency is reported to be in the order of O< N< S< P (Zhang and Hua, 2009; Usman et al., 2014,). A lot of work has been reported on the use of heterocyclic compounds used as corrosion inhibitors. The use of heterocyclic containing sulphur has been widely investigated by many researchers. Many corrosion inhibitors are found to be effective in mild steel while others are found to be toxic, highly cost and non-eco-friendly(Lukovits, and Shaban, 2005; Obot and Obi-Egbedi, 2010; Yardav, et al., 2012; Sherif, 2013).

The aims of this research is to use corrosion inhibitor with low cost, nontoxic and inhibitive corrosion effectively. In our previous study, it has been reported that thiophene type of inhibitor are effective corrosion inhibitor use in the protection of corrosions for many metals and alloys. In this paper 2-thiophene acetyl chloride is use as corrosion inhibitor in hydrogen tetraoxosulphate (VI) acid.

Computational Method

Quantitative Structure Activity Relationship (QSAR)

The dimensional structure of the inhibitor (TAC) was initially generated and converted in to 3D structure using Chemdraw in order to develop the QSAR model. Molecular descriptors for the model building were generated using Dragon Software and uploaded into a Matlab 7.9 for the model building as describe by Usman et al, (2014).

Theoretical Calculations

Density functional theory (DFT) is used in many applications to evaluate the performance of the inhibitor and inhibitor surface behaviour (Gece, and Bilgiç, 2010). In this study geometrical optimization of TAC were carried out using DFT / B3LYP method with basis set 6-311G++ (d,p) by using Gauss View 09 (Lee, et al., 1988 ; Becke, 1993; Usman et al., 2014; Wang et al, 2014). The optimised geometry was used to calculate the quantum chemical descriptors to find the ionization potential (IP) and electron affinity (EA). The structure of TAC is presented in Figure 1.

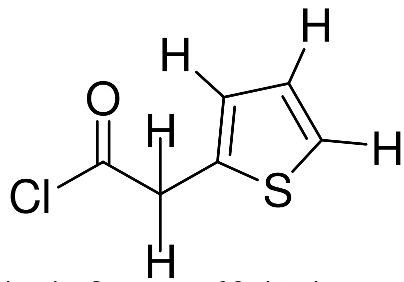

Figure 1: Molecular Structure of 2-thiophene acetyl Chloride

MATERIALS AND METHODS

Materials

The mild steel consist of used 0.036 wt%, 0.172 wt% Mn, 0.152 wt% P, 0.10S, 0.009Si, 0.082Cu^{2+}, 0.108 Ni_2, 0.001 V, 0.006Mo, 0.019Ti, 0.035Al, 0.146 Zr, 0.001B_2, 0.001B, 0.006Sb, 0.008 Co, 0.019,Sn, 0.012Sn_2, 0.005Pb and the rest is iron (Fe), from Glow discharge spectroscopy.

Solutions

The acid solutions was prepared by diluting 28 ml of H_2SO_4 with distilled water in a 1000ml volumetric flask to obtained was 0.5M H_2SO_4. The stock solution of 2-thiophene acetyl chloride was prepared by diluting 10^{-2}M of TAC in 250 ml volumetric flask with 0.5M H_2SO_4.

Potentiodynamic Polarization

The experimental was carried out using potentiodynamic polarization (PDP) using Auto lab PGSTAT 3.0 model which consist of electrode i.e. working electrode (WE), reference electrode (RE) and counter electrode (CE). The polarization study was carried out on mild steel. Sample was prepared on the dimension (2cm x 2cm x2mm). The mild steel sample was ground and polished with emry paper of different grade size of 240, 400, 600, 1000, 1200 and 1800 respectively. The sample was then washed with distilled water rinse with acetone it then dried in a hot air and kept in desiccator before its use. The polarization study was analyseusing different parameter such as Scan rate of 5mV$s^{-1}$with potential of range of 250 mV at open circuit current (OPC), with a study time of 15 minutes. And the percentage inhibition efficiency was calculated using equation (1)

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

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

Surface Characterization

The micrograph of mild steel without and with inhibitor was analysed using Field emission Scanning Electron Microscopy couple with Energy Disperse Spectroscopy as (FESEM-EDX) and the images were captured at magnification of 100μm.

RESULTS AND DISCUSSION

The properties of the compound 2-thiophene acetyl chloride were generated using Dragon software and use to build the QSAR model as describe elsewhere (Usman et al.2014) and the descriptors are presented in Table 1.

Table 1: calculated molecular descriptor

Molecular Descriptors	Values
MATS4M	0.418
SpMax3_Bh(m)	2.702

QSAR model was developed using Partial Least Square Analysis by using equation (2), which contain two properties in order to obtain a robust and reliable model.

% IE = -88.241 + (-9.881 (MATS4M) 241 +57.272 (SpMax3-Bh (m) (2)

R^2 = 0.9255, R^2_{cv} = 0.8481, R^2_{pred} = 0.5114 , RMSEC= N = 11.

The parameters R^2, R^2_{cv}, $R^2_{pred,}$ RMSEC and N are regression coefficient, regression coefficient of cross validation, regression coefficient of prediction, Root mean square error calibration and number of compound respectively.

From the model the value of R^2 , R^2_{cv} , R^2_{pred} RMSEC are found to be good. The properties are edge adjancy (MATS4M) and is used to describe the efficiency of compound to be good corrosion inhibition based on the effect of branching and molecular density (SpMax3-Bh (m) (Usman et al; 2014). Therefore, the model predicted the inhibition ability of TAC is 61.6 % presented in Table 2.

Table 2: Theoretical %IE 2-Thiophene acetyl chloride

Compound	%IE
TAC	61.6

Quantum Chemical Calculations

The structure of optimize TAC is presented in Figure 2.Quantum chemical calculation is generally used to investigate the reaction process mechanism which has been confirmedand found to be promising method to protect corrosionactivity of any compounds in relations to electronic structure(Lukovits and Shaban, 2005; , Leberi et al, 2005; Atta, et al, 2013). Therefore, the study of corrosion inhibition ability of 2-thiophene acetyl chloride has been investigated.

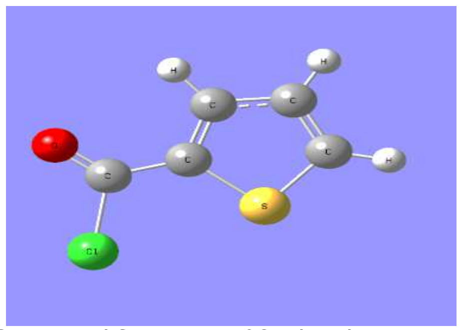

Figure 2. Optimized Structure of 2 –thiophene acetyl chloride

The value of quantum chemical properties are presented in Table 3. The quantum chemical properties are E_{HUMO}, E_{LUMO}, Egap (E_{HUMO}-E_{LUMO}) , X (Electronegativity) Electron affinity(A), Softness (S), Hardness(H) and Total Energy (TE). In measuring the corrosion performance of any organic compound frontier orbitals energy plays a significant role in explaining the reactivity of chemical compound (Ebenson et al, 2010). The E_{HUMO} , E_{LUMO} , E_{gap} and μ of TAC are found to be -0.263 , -0.103, 0.160au and 4.483debye , E_{HUMO} is responsible for the denoting ability of electron by the compound, the higher the E_{HUMO} the better the denoting ability of the compound, while lower E_{LUMO} is responsible for the mild steel to accept electron to the empty d- orbital of the inhibitorand lower E_{gap} increases the corrosion efficiency similarly, μ is responsible for the measurement of polarity of the covalent bond and distribution of charges which allow the molecules to be adsorbed on to metals surface hence TAC is a good corrosion inhibitor.

Table 3: Quantum chemical descriptors for 2-thiophene acetyl chloride

Compounds	Quantum chemical parameters			
	E_{HUMO} (au)	E_{LUMO} (au)	Egap (au)	μ (Debye)
2-thiophene acetyl chloride	-0.263	-0.103	-0.160	4.48

Other quantum chemical properties values which explain the potential of TAC as corrosion inhibitor are electronegativity (X) with the value of 0.226 au explaining how the molecule attract the electron toward itself and higher electronegativity lead to better inhibition efficiency TAC gives better inhibition efficiency. The ionization energy (I), hardness (η) , softness (S), electron affinity(A) and Total energy (TE) were calculated and found to be 0.263, 0.211, 4.737, 0.103 and -1126.1 au were calculated and presented in Table 4 respectively. The ionization and electron affinity explain the nature of compound based on electron density in which higher E_{HUMO} gives lower ionization energy and electron affinity and it lead to the better inhibition efficiency hence TAC is a better inhibitor to corrosion on mild steel.

Also the hardness and softness presented in Table 3 were confirmed and shows the molecular stability and reactivity of the compound and are found to be favourable towards corrosion protection on mild steel. However, the TE is responsible for the stability of the inhibitor, higher value of TE indicates stability of the compound to form complex with inhibitor(Soliman, et al., 2014).

Table 4: Quantum chemical parameters of 2-thiophene acetyl chloride

Compounds	Quantum chemical parameters					
	X (au)	η (au)	S (au))	I(au)	A (au)	TE(au)
2-thiophene acetyl chloride	0.226	0.221	4.737	0.263	0.103	--1126.1

X= Electronegativity, η = hardness, S = Softness, I = Ionization energy, A= Electron Affinity, TE= Total Energy

Potentiodyamic Measurement

The potentiodynamic measurement were carried out, Figure 3. Shows the polarization curve which explain the corrosion inhibition by cathodic and anodic region for mild steel in 0.5M H_2SO_4 in the presence of 0.002M TAC at 30°c for Ihr.The results calculated for different electrochemical properties are presented in Table 4. From the polarization curves the presence of TAC shows the value of anodic region is higher than the cathodic region indicating the inhibitory effect is anodic. There is change in the E_{corr} and I_{corr} for both blank and in the presence of inhibitor the given as -453, -675 $mAcm^{-2}$ and 783.3, 268.1$\mu A/cm^2$ respectively. The behaviour demonstrated that TAC is a moderate corrosion performance with 65.8% inhibition efficiency as shown in Table 4.

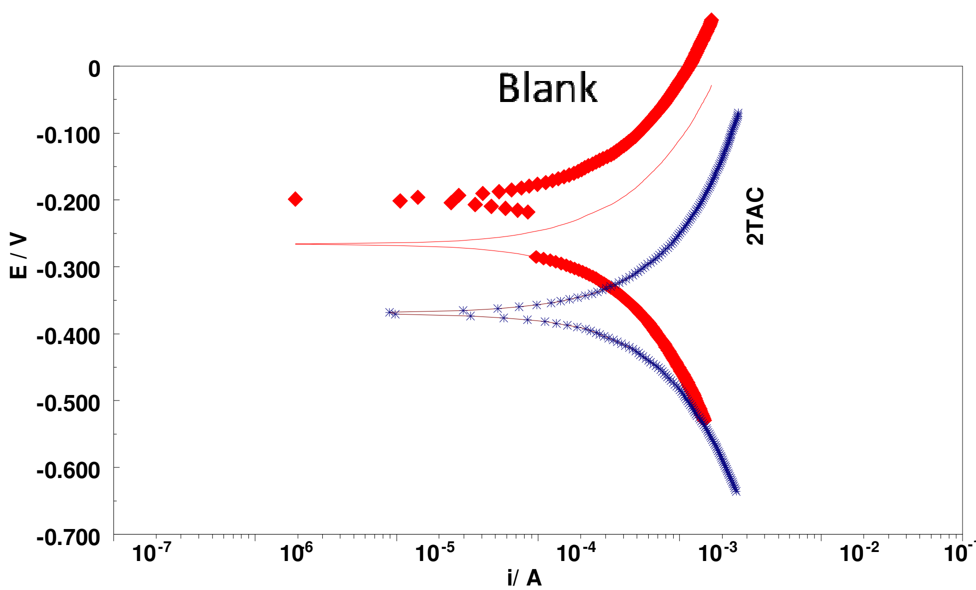

Figure 3; Polarization curve s at 30°C in (a) 0.5M H_2SO_4 (b) Presence of 0f 0.01 TAC

Table 4: Polarization data of mild steel in 0.5MH_2S0_4 with and without addition of inhibitor at 303k for 2-thiophene Acetyl Chloride

Compound	C(M)	E_{corr} ($mAcm^{-2}$)	-ba (mVdec)	-bc/mVdec.	C.R (mm/year)	I_{corr} ($\mu A/cm^2$)	%IE
Blank	0.5	-453	427	443	9.098	783.3	-
TAC	10^{-2}	-675	890	140	3.11	268.1	65.8

Surface Analysis

Fig. 3a shows an FESEM – micrograph of mild-steel immersed for I hr in 0.5 MH_2SO_4 in the absence and presence of 0.002M TAC at room temperature. The morphology in Fig.3a shows a rough surface, characteristic of the uniform corrosion of MS in acid. In the presence of TAC (Fig. 3B and C), a smooth surface can be observed, indicating that the surface was protected by the inhibitor. However, Fig. 3c shows the FESEM –EDX dot mapping and it indicatethe protective film formed on the mild steel surface in the presence of the inhibitor atomsthese results are in agreement with the Theoretical results and electrochemical experiments, wherein an inhibition performance was observed.

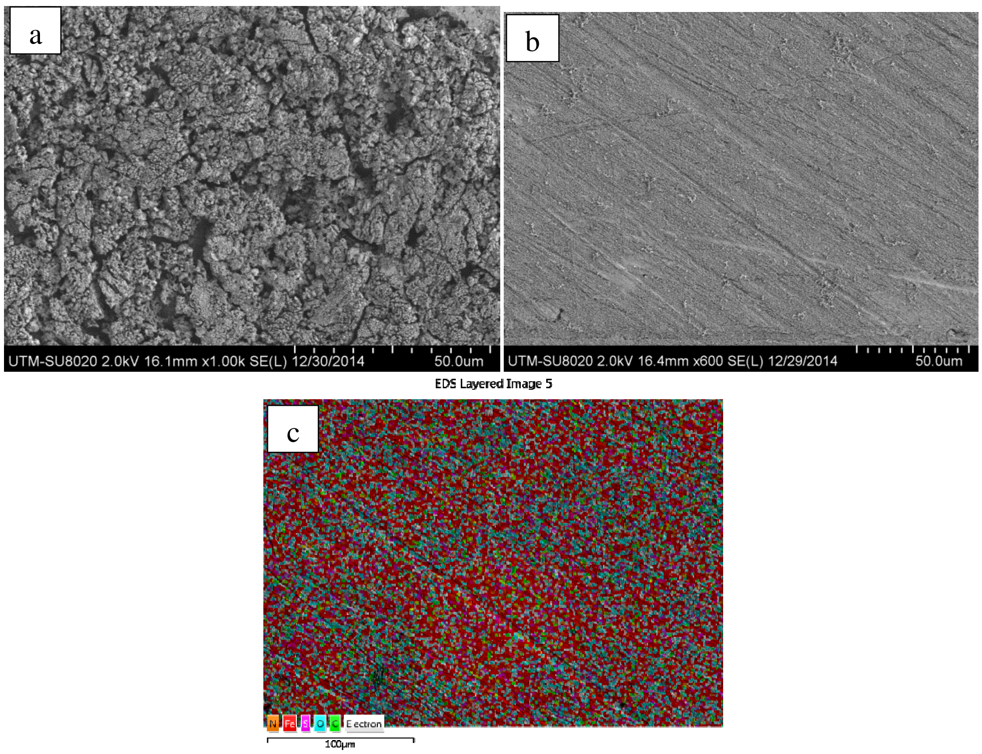

Figure 3: FESEM Micrograph (a) Blank (b) A mild in the presence of TAC (c) FESEM – EDX dot Mapping of all element on the mild steel surface

CONCLUSION

The inhibitor 2-thiophene acetyl chloride isan effective inhibitors on mild steel in0.5 M H_2SO_4solution. Theoretical result from QSAR and quantum chemical calculation found to be good. The results obtained from the polarization curves demonstrate that the thiophene act as inhibitors through an adsorption process reducing the anodic and cathodic current densities, with predominant cathodic effectiveness. The FESEM-EDX image showed that the metal surface was protected in the presence of the TAC .Theoretical calculations were in agreement with the experimental results and showed that TAC have interesting molecular structures for inhibiting the corrosive process.. The sulphur atom play an important role in the inhibition process of the thiophene derivatives for mild steel corrosion in acid medium.

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