ELECTROCHEMICAL STUDIES OF THIOSEMICARBAZONE DERIVATIVE AND ITS TIN(IV) COMPLEX AS CORROSION INHIBITOR FOR MILD STEEL IN 1 M HYDROCHLORIC ACID

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Abstract. The inhibitive effects of 2-acetylpyridine-4-ethyl-3-thiosemicarbazone (HAcETSc) and dichlorophenyltin(IV) 2-acetylpyridine-4-ethyl-3-thiosemicarbazone (Sn(HAcETSc)PhenCl$_2$) for mild steel in 1 M HCl solution at different concentrations were investigated using electrochemical measurements and scanning electron microscopy (SEM) analysis. The result of electrochemical measurement found that the inhibition efficiency increased with inhibitors' concentration. Polarisation data showed that the maximum inhibition efficiencies of HAcETSc and Sn(HAcETSc)PhenCl$_2$ were 71.31% and 88.44% respectively. Moreover, both inhibitors were categorised into a mixed-type inhibitor based on polarisation data. The electrochemical impedance spectroscopy (EIS) data showed that the maximum inhibition efficiencies of HAcETSc and Sn(HAcETSc)PhenCl$_2$ were 64.80% and 87.81% respectively. The adsorption process of inhibitor on mild steel follows Langmuir adsorption isotherm with values of R^2= 0.954 and R^2= 0.992 for HAcETSc and Sn(HAcETSc)PhenCl$_2$, respectively. The Gibbs free energy of adsorption gave a negative value, -3.76 kJ mol^{-1} for HAcETSc and -3.57 kJ mol^{-1} for Sn(HAcETSc)PhenCl$_2$ which indicated that the adsorption process occurred spontaneously and the compounds were adsorbed by the process of physical adsorption on the metal surface. SEM studies revealed that the protective film formed on the mild steel surface agreed with the result shown in EIS. The results clarified that Sn(HAcETSc)PhenCl$_2$ had a better inhibitive effect than HAcETSc.

Keywords: 2-acetylpyridine, thiosemicarbazone, tin(IV) complex, mild steel, corrosion.

Introduction

Corrosion is the destruction of metal that causes an universal environmental problem. Corrosion occurs naturally by a chemical and/or electrochemical reaction with the surrounding and it cannot totally be stopped but its reaction rate can be controlled or slowed down to lessen the corrosion process [1,2]. Apart from that, acid solution that is widely used by industrial sectors helps to remove undesirable scale and rusts (pickling of steel), which cause degradation of metal and leads to huge financial losses to repair and replace the corroded materials [3,4]. So, one of the methods to overcome the corrosion problem is by using a corrosion inhibitor. The mechanism that occurs on mild steel in acid media is the ability of inhibitor to adsorb on the metal surface, which forms a protective barrier against an aggressive attack by the corrosive agent like hydrochloric acid [5,6].

The study of green corrosion inhibitors is an attractive field for many researchers because of its usefulness in various industries such as in petroleum production, steel pipeline- making industry, refrigeration industry, automobile, paint industry, acid-producing companies, acid cleaning, acid descaling and oil well acidizing. Most researchers are focusing on a corrosion inhibitor containing electronegative atoms such as N, S, O and an aromatic group in their structure [7,8]. This is because these atoms can adsorb onto the metal surfaces and block the available reaction site from the attack of corrosive media thus reducing the rate of corrosion. There are several reports showing that thiosemicarbazone derivatives and the organotin complex act as effective corrosion inhibitors for mild steel in acidic media [9-11]. Thiosemicarbazones have been reported to give a good inhibition since the structure contains heteroatoms with free electron

pairs as well as conjugated double bond that can facilitate the adsorption on mild steel [12-14]. Meanwhile, organotin is known to have corrosion-inhibiting characteristics since it has biocidal behaviour, friction and wear reducing properties [15].

The present study aimed to investigate the corrosion inhibition effect for mild steel in 1 M hydrochloric acid of synthesised compounds namely the 2-acetylpyridine 4-ethyl-3-thiosemicarbazone (HAcETSc) and dichlorophenyltin(IV) 2-acetylpyridine-4-ethyl-3-thiosemicarbazone (Sn(HAcETSc)PhenCl$_2$) by using potentiodynamic polarisation, electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM).

Experimental

Synthesis of the thiosemicarbazone compounds

The 2-acetylpyridine 4-ethyl-3-thiosemicarbazone (HAcETSc) (Figure1*(a)*) synthesis was performed by mixing 10 mL of an ethanoic solution of 2-acetylpyridine (1 mmol) and 10 mL of an ethanoic solution of 4-ethyl-3-thiosemicarbazide (1 mmol) [16]. Then, two drops of acetic acid were added to the mixture. The mixture was refluxed for 2 hours at 60-70°C with constant stirring. After 2 hours, the solution was cooled at room temperature. The crystalline product obtained from slow evaporation at room temperature was filtered, washed with cold ethanol and dried over anhydrous silica gel.

The organotin complex dichlorophenyltin(IV) 2-acetylpyridine-4-ethyl-3-thiosemicarbazone (Sn(HAcETSc)PhenCl$_2$) (Figure 1*(b)*) was obtained by stirring the reaction mixture of synthesised ligand that was firstly dissolved in 10 mL of ethanol [17]. The metal salt, phenyltin(IV) trichloride (1 mmol) was dissolved in 10 mL of distilled water with a molar ratio of 1:1 (ligand:metal salt). The metal salt was added drop-wise to the ethanoic solution ligand with constant stirring. The reaction mixture was continuously stirred for 4 hours. The product was then filtered and washed with 10 mL of cold ethanol.

Study of anti-corrosion properties of thiosemicarbazone compounds
Electrochemical measurements

The steel used in this study was mild steel with a chemical composition of C- 0.34%, Mn- 0.76%, P- 0.02%, Si- 0.3%, and the balance Fe. For all of the experiments, the mild steel was polished with a series of emery paper silica carbide paper grades from 320 to 1200. After that, the specimen was washed with distilled water and degreased with acetone samples. Finally, the mild steel was dried at room temperature before use. The aggressive solution of 1 M HCl was freshly prepared by dilution with distilled water of 37% analytical grade HCl.
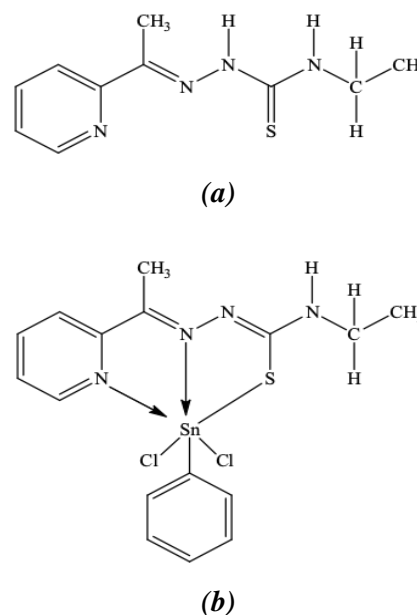

(a)

(b)

Figure 1. Chemical structure of HAcETSc *(a)* and Sn(HAcETSc)PhenCl$_2$ *(b)*.

The electrochemical measurements such as *electrochemical impedance spectroscopy (EIS)* and *Tafel polarisation* studies were conducted to evaluate the corrosion inhibition performance of synthesised inhibitors on the mild steel by using alternative current (AC) and direct current (DC) signals, respectively. The electrochemical measurements were performed by using the Autolab Potentiostat (Aut302 FRA 2) where a PC was controlled with the NOVA software. The analysis was performed by a three-electrode system that contained a platinum rod as a counter electrode, silver-silver chloride (Ag/AgCl) as a reference electrode and mild steel as a working electrode. The working electrode was prepared by embedding the mild steel in epoxy resin and exposing the surface area of 0.1 cm^2 to the test solutions containing various concentration of inhibitor (0.1 mM, 0.5 mM, 1.0 mM, 1.5 mM and 2.0 mM). This measurement was conducted at 25°C by immersing the working electrode in the test solution unstirred for about 10 minutes over open circuit potential (OCP) to provide sufficient time to attain a stable value.

The impedance analysis was conducted in the frequency range of 10 kHz to 0.1 Hz at open circuit potential by applying peak-to-peak amplitude AC signal of 0.01 V. The percentage of corrosion inhibition efficiency from EIS studies

was calculated by using the following formula, Eq.(1) [18]:

$$IE_{EIS}(\%) = \frac{R_p^o - R_p}{R_p^o} \times 100 \qquad (1)$$

where, R_p^o and R_p are the polarisation resistances with and without the inhibitor, respectively.

The *Tafel polarisation measurements* were carried out immediately after performing the EIS measurement by using the same working electrode without applying any additional surface treatment [19]. The potential values were scanned in the potential range from -100 mV to $+100$ mV versus corrosion potential at a scan rate of 0.001 V s^{-1} [20]. The percentage of inhibition efficiency from Tafel polarisation study was calculated by using the following formula, Eq.(2) [21]:

$$IE_{pol}(\%) = \frac{i_{corr}^o - i_{corr}}{i_{corr}^o} \times 100 \qquad (2)$$

where, i_{corr}^o and i_{corr} are the current density without and with inhibitor, respectively.

Scanning electron microscopy study

The surface morphology study was conducted by using Tabletop Hitachi TM3030Plus. The energy of the acceleration beam employed was 20 kV. The scanning electron microscopy (SEM) analysis was carried out on the mild steel surfaces of samples that were immersed for 24 hours in the acidic solutions without and with the optimal concentration of inhibitor.

Adsorption and thermodynamic studies

Adsorption of the inhibitor on the mild steel was assumed as an essential part of the mechanism in the corrosion inhibition process. In order to determine the adsorption mode, the degree of surface coverage (θ) of the inhibitor is calculated with several adsorption isotherms, including Langmuir, Frumkin, and Temkin. In this study, the degree of surface coverage values (θ) for various concentrations (0.1 mM, 0.5 mM, 1.0 mM, 1.5 mM and 2.0 mM) of the inhibitor in acidic media was evaluated from polarisation values. The Langmuir adsorption isotherm was found to best fit the adsorption behaviour of the investigated inhibitor where the linear regression coefficient value (R^2) is very close to 1. Langmuir's isotherm is expressed as follows, Eq.(3) [22]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (3)$$

where θ- the fractional surface coverage;
C_{inh}- the inhibitor concentration;
K_{ads}- the equilibrium constant of the adsorption process. K_{ads} is related to the standard Gibbs free energy of adsorption (ΔG°_{ads}) through Eq.(4) [23].

$$\Delta G_{ads} = -RT(\ln 55.5 K_{ads}) \qquad (4)$$

where, R- the universal gas constant (8.314 J K^{-1} mol^{-1});
T- the temperature in kelvins (298 K);
the factor 55.5 M is the molar concentration of water in the solution.

Results and discussion
Electrochemical impedance spectroscopy results

The semi-circle Nyquist plots obtained from the experiment can be model by a simple Randle's circuit (Figure 2), which showed that the charge transfer resistance (Rp) was parallel with the constant phase element (CPE) in series with solution resistance (Rs) [24].
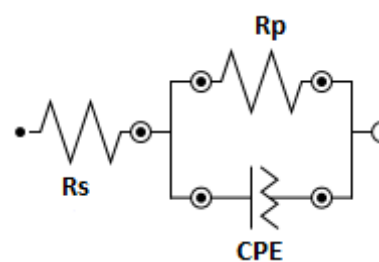

Figure 2. Simple Randle's circuit.

The Nyquist plots for the mild steel in different concentrations of HAcETSc and Sn(HAcETSc)PhenCl$_2$ in 1 M HCl are shown in Figure 3(a) and (b), respectively. The Nyquist plot showed a deviation from ideal semicircles which were referred as frequency dispersion and the result of the non-homogeneity or roughness of the metal surface and mass transport resistance [25,26]. The diameter of the semi-circle curve increased when the inhibitor concentration increased, proving the existence of the adsorption of the inhibitor on mild steel [27]. Hence, this provided corrosion inhibition on mild steel whereby the formation of adsorbed layer created a barrier for charge and mass transfers at the metal-inhibitor solution interface [28]. The impedance parameters obtained are tabulated in Table 1.
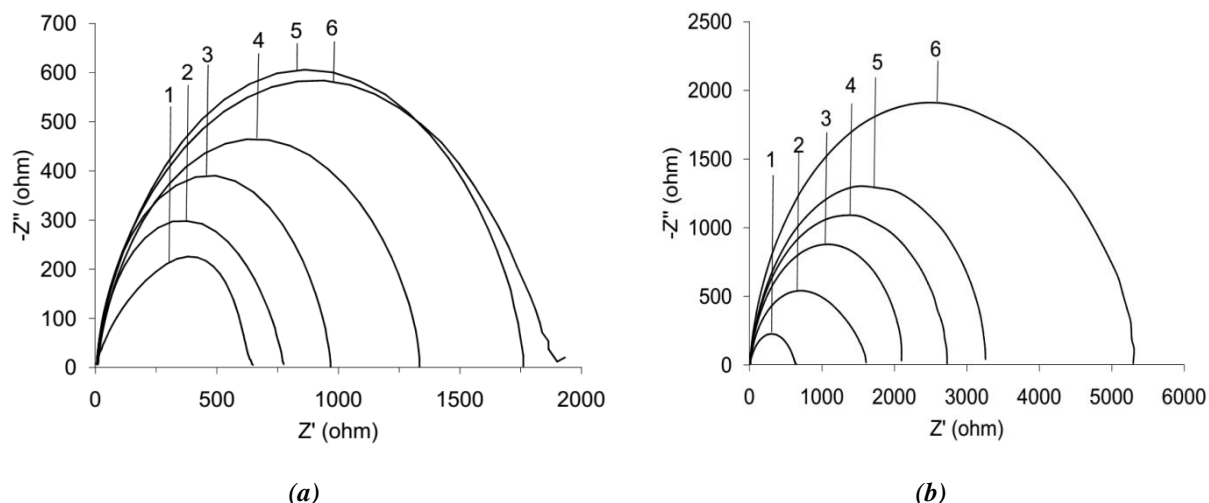
(a) (b)

Figure 3. Diagram for mild steel with various concentration of HAcETSc (a) and Sn(HAcETSc)PhenCl$_2$ (b).
1- Blank, 2- 0.1 mM, 3- 0.5 mM, 4- 1.0 mM, 5- 1.5 mM, 6- 2.0 mM.

Table 1

Impedance parameter values.

Inhibitor	Concentration (mM)	Rs (ohm cm^{-2})	Rp (ohm)	IE$_{EIS}$ (%)
Blank	1M	0.59	630	-
HAcETSc	0.1	0.90	739	14.7
	0.5	0.48	937	32.7
	1.0	0.77	1300	51.5
	1.5	0.25	1700	62.9
	2.0	0.24	1790	64.8
Sn(HAcETSc)PhenCl$_2$	0.1	1.09	1520	58.5
	0.5	0.69	2080	69.7
	1.0	0.36	2710	76.7
	1.5	0.27	3270	80.7
	2.0	0.44	5170	87.8

Rs - solution resistance;
Rp - charge transfer resistance;
IE$_{EIS}$ – inhibition efficiency.

As seen in Table 1, the *Rp* values substantially increased along the concentration, which can be deduced to the formation of the protective film on the metal-inhibitor solution interface [29]. Apart from that, the large value of *Rp* indicated a slower corrosion system [30]. The best corrosion inhibition efficiency recorded by EIS was 87.81% at the concentration of 2 mM by the inhibitors Sn(HAcETSc)PhenCl$_2$.

Tafel polarisation results
Table 2 presents the potentiodynamic polarisation parameters which are corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), corrosion rate (*CR*), and inhibition efficiency

(IE_{pol}) for mild steel in 1 M HCl with and without inhibitors. Tafel polarisation curves for mild steel in 1 M HCl solution in the absence and presence of various concentrations of the inhibitors HAcETSc and Sn(HAcETSc)PhenCl$_2$ are as seen in Figure 4(a) and (b) respectively. The optimum corrosion inhibition efficiency recorded by the polarisation result was 88.44% at the concentration of 2 mM by the inhibitor Sn(HAcETSc)PhenCl$_2$. Polarisation measurements revealed that both inhibitors, HAcETSc and Sn(HAcETSc)PhenCl$_2$ were mixed type inhibitors because their displacement corrosion potential (E_{corr}) against the blank was less than 85 mV [31].

Table 2

Polarisation parameter values.

Inhibitor	Concentration (mM)	i_{corr} ($\mu A\ cm^{-2}$)	E_{corr} (mV)	β_a (mV dec^{-1})	β_c (mV dec^{-1})	CR (mm/yr)	IE_{pol} (%)
Blank	1M	330.64	-423.65	156.53	71.916	3.842	-
HAcETSc	0.1	201.22	-482.07	153.83	51.348	2.3382	39.1
	0.5	206.75	-481.97	177.83	63.856	2.3303	39.3
	1	144.44	-460.61	171.43	63.944	1.6784	56.3
	1.5	101.09	-461.58	171.49	59.726	1.1747	69.4
	2	94.861	-458.11	164.06	61.444	1.1023	71.3
Sn(HAcETSc)PhenCl$_2$	0.1	77.95	-451.10	217.29	30.017	0.9057	76.4
	0.5	74.116	-443.04	9023.8	23.696	0.8612	77.5
	1	73.721	-440.89	757.01	35.203	0.8566	77.7
	1.5	62.64	-428.82	321.10	39.382	0.7278	81.0
	2	38.231	-353.11	647.90	53.49	0.4442	88.4

i_{corr} -corrosion current density;
E_{corr} -corrosion potential;
β_a -anodic Tafel slope;
β_c -cathodic Tafel slope;
CR -corrosion rate;
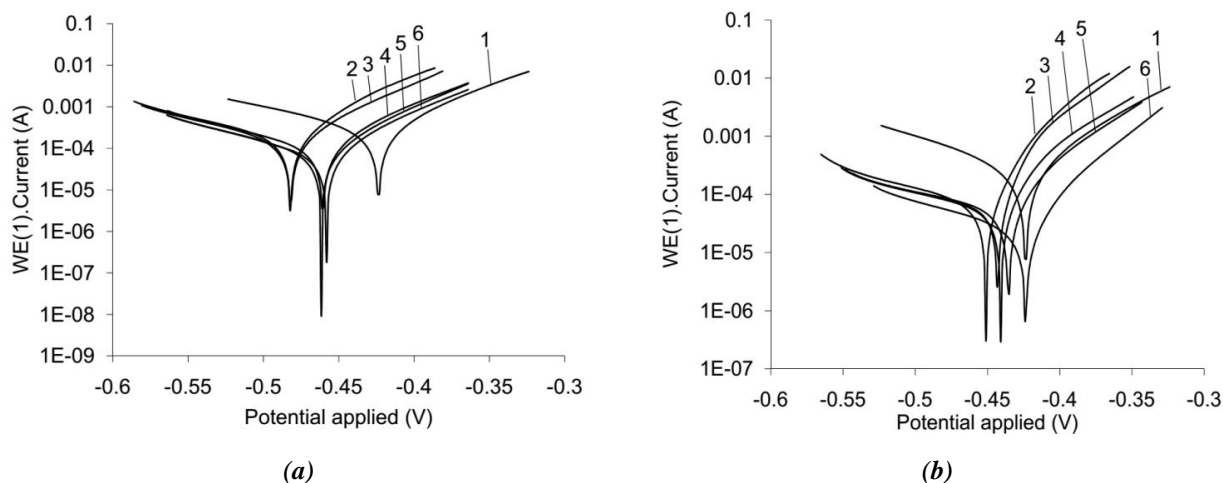IE_{pol} -inhibition efficiency.

(a)   *(b)*

Figure 4. Tafel polarisation curve of mild steel with various concentration of HAcETSc *(a)* and Sn(HAcETSc)PhenCl$_2$ *(b)*. *1*- Blank, *2*- 0.1 mM, *3*- 0.5 mM, *4*- 1.0 mM, *5*- 1.5 mM, *6*- 2.0 mM

In the present study, the values of E_{corr} show irregular trends. The maximum displacement is 70.54 mV with respect to the blank value which indicates a mixed type behaviour of inhibitors. This result also suggested that mild steel was simultaneously inhibited by the inhibitors through anodic and cathodic reactions by reducing the anodic dissolution and also retarded the hydrogen evolution reaction [32]. The higher value of β_a as compared to β_c of the inhibitor from different concentrations suggested that the inhibitor predominantly suppressed the anodic reaction. The i_{corr} decreased when the concentration of inhibitor increased

[33]. This indicated the inhibiting effect of both inhibitors on the aggressive solution of the mild steel which caused effective blockage of the active site when the inhibitor was being adsorbed on the mild steel surface [34,35]. The β_c values show a slight change with increasing inhibitor concentration, which indicates the effect of the inhibitor on the kinetics of hydrogen evolution. Further observation on the Tafel slopes is where the magnitude of shifting in the anode is higher than in the cathodic direction. The cathodic direction does not change significantly. This explains that the anodic reaction is more drastically inhibited compared to the cathodic

reaction. One can conclude that the inhibitors act as a mixed type with predominant anodic effect. According to Ismail, A. anodic inhibitors cause a large anodic shift of the corrosion potential and it is inhibited by forming a protective oxide film on the surface of the mild steel [36]. In conclusion, the cathodic curves which demonstrate that adding an inhibitor the corrosive environment does not modify the mechanism of hydrogen evolution and the recovery of H^+ ions on the surface of mild steel, follow the charge transfer mechanism.

SEM results

The SEM analysis was performed to study the mild steel surface in the absence and presence of inhibitors. Figure 5(a) shows the micrograph for the mild steel surface that had been immersed in 1 M HCl in the absence of inhibitors (blank), Figure 5(b) shows the mild steel surface inhibited with HAcETSc and Figure 5(c) shows the mild steel surface inhibited with Sn(HAcETSc)PhenCl$_2$. As shown in Figure 5(a), the mild steel surface immersed in the absence of inhibitor was damaged with deep holes on certain surfaces. This was due to the dissolution of metal in the aggressive solution. The presence of the holes on the mild steel surface suggested the occurrence of pitting corrosion [37]. Pitting marks on the surface are due to the attack of the aggressive solution in absence of inhibitors [38]. Nevertheless, in Figure 5(b) and Figure 5(c), mild steel surfaces immersed in the presence of inhibitor at high concentration show smoother surfaces due to the protective film formed on the mild steel surface which prevented the aggressive attack of the acid on mild steel [39]. The inhibitor can be adsorbed on mild steel by interaction between the mild steel and the presence of lone pair electrons in the sulphur and nitrogen atoms, π electrons on the aromatic ring, molecular size, and the formation of a metal complex. These results proved that the inhibitor Sn(HAcETSc)PhenCl$_2$ had the best inhibition performance, which agreed with the result obtained from the polarisation and impedance experiments.

Adsorption study

The results show that the adsorption mechanism of HAcETSc and Sn(HAcETSc)PhenCl$_2$ on mild steel was suitable with the Langmuir isotherm model where the plot of the straight line gave $R^2 = 0.954$ for HAcETSc and $R^2 = 0.992$ for Sn(HAcETSc)PhenCl$_2$ (Figure 6). The isotherm plots suggest that the adsorption of the inhibitor on the mild steel occupy only one site and there are no interactions with other adsorbed molecules [40]. The thermodynamic study was also conducted to determine the adsorption mechanism by calculating the standard free energy of adsorption (ΔG_{ads}) [41]. The ΔG_{ads} values from the experiment were -3.76 kJ mol^{-1} and -3.57 kJ mol^{-1} for HAcETSc and Sn(HAcETSc)PhenCl$_2$, respectively. The study proved that the adsorption of both inhibitors on the mild steel surface has occurred by physisorption. In general, the physisorption involves the electrostatic interaction between the charged inhibitor molecules and the charged metal surface occurs if the energy value of ΔG_{ads} lies around -20 kJ mol^{-1} or less negative, whereas the chemisorptions in which the charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond occurs at a value around of -40 kJ mol^{-1} or more negative [42].
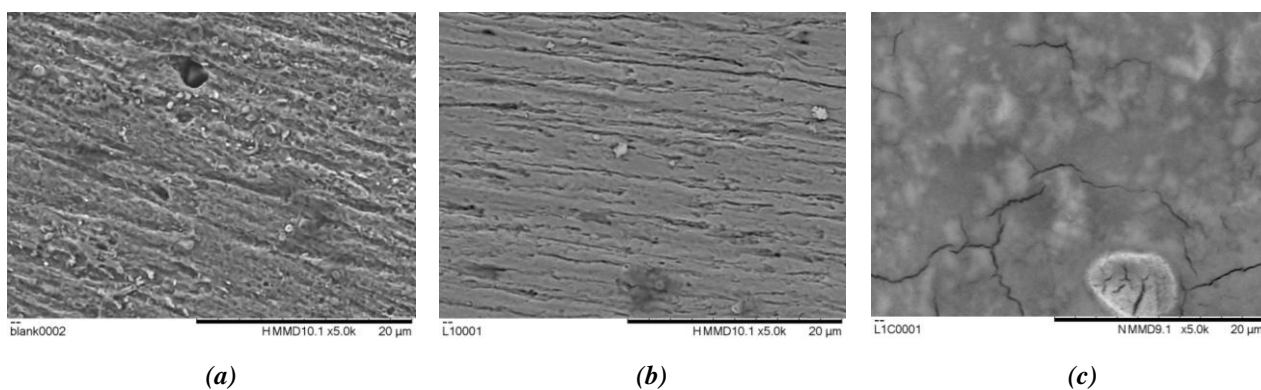

(a)   *(b)*   *(c)*

Figure 5. SEM images of uninhibited mild steel (blank) *(a)*, mild steel inhibited with HAcETSc *(b)* and mild steel inhibited with Sn(HAcETSc)PhenCl$_2$ *(c)* (magnification: 5000).
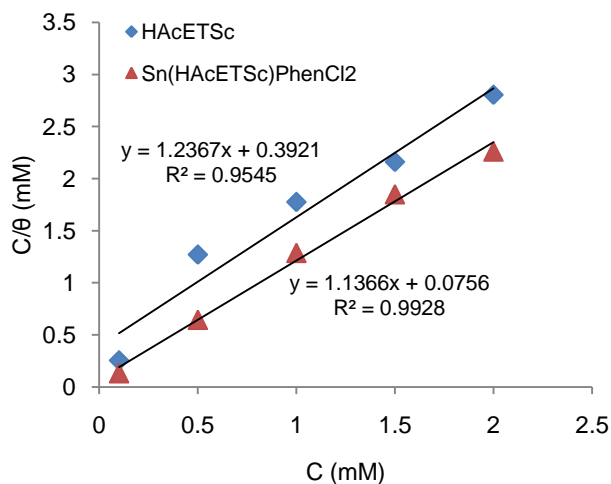
Figure 6. Langmuir isotherm for the adsorption of both inhibitors.

Conclusions

In this paper, the corrosion inhibition effect of the synthesised compounds, HAcETSc and Sn(HAcETSc)PhenCl$_2$ in 1 M HCl on mild steel was studied. The analyses from EIS and Tafel polarisation concluded that the compound Sn(HAcETSc)PhenCl$_2$ showed better efficiency than HAcETSc. Although the inhibition efficiency data of EIS and Tafel polarisation methods were not very comparable, the trend of inhibition efficiency with the variation of concentration is noticeable by the two methods. The observed trends by both EIS and Tafel polarisation methods show that the inhibition efficiency increases as the inhibitor concentration increases. The difference between these two methods occurs because of the different type of applied potential that is used. For EIS method, the electrode was under the open-circuit potential while for Tafel polarisation method, the working electrode was polarised and the electrochemical parameters were obtained by extrapolation of the Tafel lines.

The polarisation measurement showed a mixed type inhibitor where the inhibitor successfully inhibited the cathodic hydrogen evolution and anodic metal dissolution reactions. The impedance plots of inhibitor proved the formation of the protective layer on the mild steel. The results of the study were supported by SEM analysis.

The adsorption of these inhibitors on the mild steel surface in 1 M HCl solution obeyed the Langmuir's adsorption isotherm and kinetic model. The negative sign of ΔG^o_{ads} indicated that the adsorption process occurs spontaneously. The activation energy values increase when the inhibitors is added to the 1 M HCl solution indicating that physisorption is more predominant than chemisorption.

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