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Corrosion Inhibition of Mild Steel in Seawater by 2,4,6-Triamino-3-Pentadecylphenyl Acetate Derived from Cashew Nut Shell Liquid

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Abstract

The corrosion inhibition performance of 2,4,6-triamino-3-pentadecylphenyl acetate on mild steel in seawater at stationary condition, 30 °C and pH 8 was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy. The maximum inhibition efficiency of 93% was found in the presence of 300 ppm of 2,4,6-triamino-3-pentadecylphenyl acetate for both potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The potentiodynamic polarization curves show that 2,4,6-triamino-3-pentadecylphenyl acetate acts as a mixed type inhibitor which influences more the anodic processes. The Nyquist plots revealed that the polarization resistance (R_p) increases whereas the double-layer capacitance (C_{dl}) and corrosion current density (i_{corr}) decrease as the concentrations of the inhibitors increase due to the formation of a protective layer of inhibitor over the mild steel surface. The results obtained from the two electrochemical techniques are in good agreement. The adsorption of 2,4,6-triamino-3-pentadecylphenyl acetate on the mild steel surface obeyed Langmuir adsorption isotherm.

Keywords: Cashew nut shell liquid; 2,4,6-triamino-3-pentadecylphenyl acetate; corrosion inhibitor; mild steel; seawater.

Introduction

Mild steel is an alloy of iron and carbon in which the carbon content is between 0.15 to 0.20% (Li et al 2018). Steel materials are common construction materials in buildings, bridges, pipelines, tanks, boilers, tubing, borehole, casing, valves and pumps (Finšgar and Jackson 2014). However, these materials are highly susceptible to corrosion when they are exposed to operating environments (Aldana-González et al. 2019).

In the oil and gas industry, mild steels are used for the construction of tanks and pipelines, for storage and transport of petroleum products (Migahed et al. 2005). The internal parts of the tanks and oil pipelines are

in contact with hydrocarbons and corrosive agents such as CO₂, H₂S, Cl⁻, SO₄²⁻, H₂O and dissolved O2 (Popoola et al. 2013). Since mild steel corrosion causes serious problems including an increase in the total production costs, loss of product, reduced safety and environmental pollution (Hussin and Kassim 2010), it is worthy to investigate different ways of preventing or minimizing mild steels corrosion. Generally, metal corrosion mitigation methods include suitable engineering design, the applications of passive alloys, metal surface amendments galvanizing and electroplating), electrical control (e.g., anodic protection), electrochemical technique (e.g., cathodic

modification αf the protection) and environments in contact with the metallic structure (e.g., pH regulation, elimination of corrosive species and the use of corrosion inhibitors) (Philip et al. 2016). Among these techniques, the use of corrosion inhibitors seems to be more versatile, practical and economical in transportation and storage systems. Corrosion inhibitors are chemical substances that can be applied in small amounts to the operating environment of the mild steel, to protect the mild steel surface against corrosion (Bagavathy and Ganesan 2015). In accordance with the increasing safety and environmental concerns, the development of cheap, readily available, effective, non-toxic and environmentally friendly corrosion inhibitors from natural sources is of great demands (Kumpawat et al. 2012, Sribharathy et al. 2013, Shalabi et al. 2014, Tang 2019).

The plant extracts contain varieties of chemical compounds such as essential oils, pigments, tannins, terpenes, steroids, flavonoids, flavones, among others, which are reported to be effective corrosion inhibitors (Sastri 2011). These compounds can be used directly as corrosion inhibitors or chemically modified to achieve the desired corrosion inhibition properties. In this study, Cashew Nut Shell Liquid (CNSL) was used as a raw material to prepare the targeted inhibitor. The CNSL is a by-product of the cashew industry; it is obtained from the cashew (Anacardium occidentale Linn) nutshells. CNSL is one of the sources of naturally occurring phenols. Its phenolic compounds have an alkyl side chain (C_{15}) with varying degrees of saturation (saturated, monoene, diene and triene). Due to properties, structural the components of the CNSL are prone to a variety of chemical reactions leading to the industrially important chemical compounds including dyes, laminating resins, compounding resins, surfactants, epoxy resins, insecticides, oil additives and anticorrosivepaints (Gedam and Sampathkumaran 1986, Gandhi et al. 2013).

The major component of natural CNSL is anacardic acid (1). Other compounds are cardanol (2), cardol (3), and a trace amount of 2-methylcardol (4). It was envisaged that from CNSL, one can chemically modify anacardic acid (the major component of CNSL) to 2,4,6-triamino-3-pentadecylphenyl acetate, anticipated to serve as a corrosion inhibitor on mild steel surface in aqueous media. Therefore, the present study aimed at investigating the corrosion inhibiting properties of 2,4,6-triamino-3-pentadecylphenyl acetate derived from CNSL on mild steel in seawater.

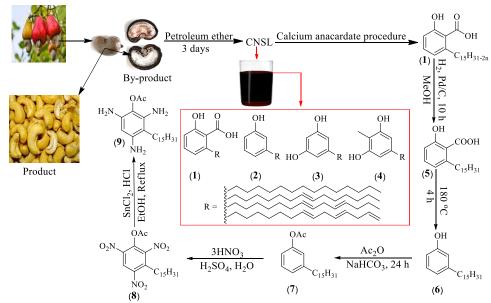
Materials and Methods Materials and instruments

All chemicals and reagents used in this work were purchased from Sigma Aldrich (South Africa). The solvents and reagents were of analytical grade and they were used as supplied. The mild steel electrodes of a circular disc with 2 mm thick and 6 mm radius were prepared from the parent mild steel oil pipeline. The cashew nut shells were collected from Mtwara region in Tanzania. The seawater (20 L) was sampled along the coastal areas of Indian Ocean in Dar es Salaam at Kigamboni Ferry terminal. The instruments used were Fourier Transform Infra-Red Spectrometer (FT-IR: Alpha ATR-BRUKER, Gmbh 2011) for characterization of the functional groups of the synthesized inhibitor; Atomic Absorption Spectrometer (AAS: Thermo Fisher Scientific iCE 3000 C113300182 v1.30) for elemental analysis in seawater; a computer-controlled potentiostat (AUTOLAB PGSTAT20 from **ECO** CHEMIE. Netherlands) potentiodynamic polarization measurements; a computer-controlled AUTOLAB Frequency Response Analyser (FRA) for Electrochemical Impedance Spectroscopy (EIS) measurements.

Preparation of the inhibitor

The corrosion inhibitor was synthesized using CNSL, as a starting material, through a series of steps abridged in Scheme 1. The extraction of CNSL (a mixture of anacardic acid (1), cardanol (2), cardol (3), and a trace

amount of 2-methylcardol (4)) from cashew nut shells was followed by isolation of compound 1, then hydrogenation of compound 1 to obtain 2-hydroxy-6-pentadecylbenzoic acid (5) followed by decarboxylation of compound 5 to obtain 3-pentadecylphenol (6). Compound 6 was acetylated to obtain 3-pentadecylphenol acetate (7) which was further treated with a nitrating agent (HNO_3 and H_2SO_4 in 5:1 ratio) to obtain 2,4,6-trinitro-3-pentadecylphenyl acetate (8). Compound 8 was treated with a reducing agent ($SnCl_2/HCl$ in ethanol) to obtain 2,4,6-triamino-3-pentadecylphenyl acetate (9), as the targeted corrosion inhibitor.



Scheme 1: Synthesis of 2,4,6-triamino-3-pentadecylphenyl acetate from CNSL as a corrosion inhibitor of mild steel in seawater.

Seawater

The electrolyte used in this work was seawater sampled along the coast of Indian Ocean near, Kigamboni Ferry terminal, Dar es Salaam, Tanzania. The sampled seawater was filtered through a Whatman filter paper and stored in a refrigerator. In the present study, the concentrations of cations Na⁺, Ca²⁺, Ba²⁺ and K⁺ were analyzed by using AAS, and the concentrations of anions Cl⁻ and SO₄²⁻ were determined by titration method.

Preparation of mild steel electrodes

The mild steel disc working electrode was prepared from the parent mild steel oil pipeline, which was previously obtained by an earlier researcher from TAZAMA Pipelines Limited - Dar es Salaam. The steel disc was wet polished

with a sequence of silicon carbide papers of decreasing particle sizes, *i.e.*, 320, 800 and 4000 grit. Thereafter, the circular working electrode was rinsed with distilled water and degreased in ethanol by sonication for about 15 minutes and afterwards rinsed with acetone and dried. The working electrode was immediately exposed to the electrolyte solution (seawater) after inserting it in an epoxy holder with Teflon O-ring, which allows exposure of a surface area of 0.79 cm².

Electrochemical cell

The electrochemical experiments were performed in a 250 mL capacity double wall Pyrex glass container. The Pyrex glass container was washed with distilled water, rinsed with acetone and air-dried before use.

The electrolyte (seawater, 250 mL) was transferred into the cell and the cell was assembled with electrodes, i.e., a working electrode, a reference electrode and a counter electrode, were inserted into the electrolyte and connected to a computer-assisted AUTOLAB PGSTAT20. The reference electrode was a saturated Ag/AgCl which was exposed to the electrolyte via Lugging capillary tube. The counter electrode was two stainless steel roads, each of 2 mm diameters. A thermometer was used for monitoring the temperature of the system and the system temperature was maintained at 303 K. The experimental set-up for the electrochemical measurements was as reported by Philip et al. (2001).

Electrochemical measurements

this study, two electrochemical In techniques, namely potentiodynamic polarization and electrochemical impedance spectroscopy were used to investigate the corrosion inhibition performance of 2,4,6triamino-3-pentadecylphenyl acetate on mild steel in seawater. The inhibition performance of the inhibitor was studied by varying the concentrations of the inhibitor. temperature was maintained at 30 °C and the measurements were performed at stationary conditions.

Measurements of open circuit potential (OCP)

The behaviour of the electrolyte solution (seawater) on mild steel was investigated before adding the corrosion inhibitor. The information obtained from the blank measurements served as a pilot for the subsequent experiments. The variation of potential with time at an open circuit was recorded by using a computer-assisted

AUTOLAB PGSTAT20 potentiostat to determine the time required for the system to attain a constant value of potential called Open Circuit Potential (OCP).

Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were performed using a computer-controlled AUTOLAB PGSTAT20 Potentiostat. The measurements were carried on the specimens by sweeping the potential at the rate of 1 mV/s in a range of 100 mV vs Ag/AgCl reference electrode cathodically and anodically from OCP. The cathodic and anodic polarization curves were taken separately, starting with the cathodic sweep. polarization measurements were performed the electrochemical impedance after measurements.

Electrochemical impedance measurements

The Electrochemical Impedance Spectroscopy (EIS) measurement was carried out by using a computer-assisted AUTOLAB Frequency Response Analyzer in the frequency range of 10 kHz to 1 mHz with a perturbation amplitude of 10 mV. The measurements were all performed at the open circuit potential and were taken after 10 h of exposure before taking the polarization measurement.

Results and Discussion

Concentration of the most abundant ions in the electrolyte (seawater)

Before the corrosion inhibition performance test, the solution chemistry of the seawater was studied to determine the corrosive agents present in the sampled seawater. The pH of seawater was found to be 8.0. The concentrations of the most abundant ions in the seawater are shown in Table 1.

Table 1: Concentration of the most abundant ions in the sampled seawater

Elemental composition	Na ⁺	Ca ²⁺	K^{+}	Ba ²⁺	Cl ⁻	SO_4^{2-}
Concentration (mg L ⁻¹)	11361.9	376.4	279.5	104.6	21263.3	2.1

Table 1 shows that the seawater contains a high content of chloride ions compared to the rest of

the ions. The chloride and sulphate ions are highly electronegative and very reactive

corrosive agents. Therefore, the presence of chloride and sulphate ions in the sampled seawater is believed to cause corrosion of mild steel.

Synthesis of the inhibitor

From 2 kg of cashew nut shells, 309.3 g (about 15.5% yield) of CNSL was extracted as a dark reddish-brown viscous liquid. Then, from 100 g of CNSL, 59.3 g (59.3% yield) of anacardic acid was isolated. From 13.6 g of anacardic acid, 12.6 g (92.6% yield) of 2-hydroxy-6-pentadecylbenzoic acid (2-H-6-

PBA) was obtained as an off-white solid with melting point range of 91.5–93.5 °C. From 7.1 g of 2-H-6-PBA, 5.7 g (80.3% yield) of 3-pentadecylphenol (3-PDP) was obtained as a dark brown liquid. From 5.0 g of 3-PDP, 4.5 g (90%) of (3-pentadecylphenyl) acetate (3-PDPA) was obtained as a reddish-brown solid. The FT-IR spectra for CNSL, anacardic acid and 2-H-6-PBA are similar to those reported in the literature (Wilson et al. 2014). The FT-IR spectral results of 3-PDP and 3-PDPA are shown in Figure 1.

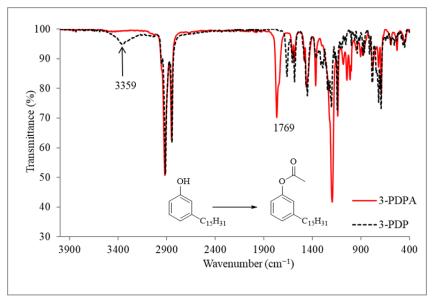


Figure 1: Combined FT-IR spectra for 3-PDP and 3-PDPA.

The FT-IR spectral results in Figure 1 show a disappearance of the absorption band at 3359 cm⁻¹ in 3-PDPA indicating that the OH group of 3-PDP was successfully acetylated. Also, Figure 1 shows the appearance of a new absorption peak at 1769 cm⁻¹ in 3-PDPA, due to formation of ester functional group after acetylation of 3-PDP. The nitration of 3-PDPA (1.2 g) gave 2,4,6-trinitro-3-pentadecylphenyl acetate as the major product. The reduction of the purified 2,4,6-trinitro-3-pentadecylphenyl acetate (1.4 g) gave 1.3 g (92.9%) of 2,4,6-triamino-3-pentadecylphenyl acetate

(TAPDPA) as a light brown solid. The FT-IR spectra for 3-PDPA and TAPDPA are shown in Figure 2.

As can be seen in Figure 2, new absorption peaks at 3459 and 3216 cm⁻¹ in TAPDPA spectrum were due to N-H stretching vibration of amine groups. The other new peak at 1544 cm⁻¹ corresponds to N-H bending vibration. Therefore, these observations confirm a successful semi-synthesis of 2,4,6-triamino-3-pentadecylphenyl acetate from anacardic acid isolated from CNSL.

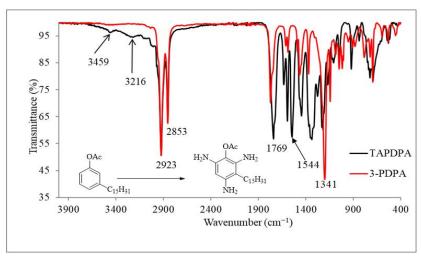


Figure 2: Combined FT-IR spectra for 3-PDPA and TAPDPA.

Electrochemical measurements Variation of OCP with time

Figure 3 shows the changes of OCP with time for the mild steel electrode immersed in seawater at 30 °C and pH 8 without inhibitor. From Figure 3, it can be seen that the open

circuit potential attained relatively constant values of potential after 10 hours exposure. Therefore, based on this information, all the electrochemical measurements were performed after ten hours exposure of the mild steel electrode in seawater at 30 °C and pH 8.

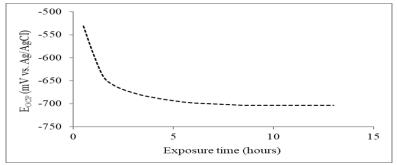


Figure 3: Variation of OCP with time for the mild steel electrode immersed in seawater without inhibitor at 30 °C and pH 8.

Potentiodynamic polarization measurements

In this technique, the current produced as a function of applied potential was measured and the measurements were taken after ten hours exposure of mild steel in seawater without and with various concentrations of 2,4,6-triamino-3-pentadecylphenyl acetate at 30 °C and pH 8. The potentiodynamic polarization curves obtained are shown in Figure 4. As seen from this figure, both anodic and cathodic current

densities decrease in the potential region studied as the concentrations of 2,4,6-triamino-3-pentadecylphenyl acetate were increased. It is also observed that as the concentrations of the inhibitor increase; the corrosion potential is shifted anodically, showing that 2,4,6-triamino-3-pentadecylphenyl acetate affects the anodic reaction predominantly than cathodic reaction. The electrochemical parameters, Tafel slopes (b_a and b_c), corrosion current densities (i_{corr})

and corrosion potentials (E_{corr}) obtained by extrapolating the Tafel lines of the polarization curves at 5 mV to 10 mV from the open circuit potential anodically and cathodically are shown

in Table 3. The calculated values of the corrosion rate (C.R) and inhibition efficiencies (IE) are also included in Table 2.

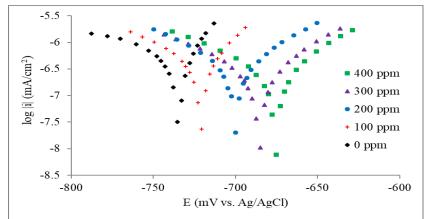


Figure 4: Polarization curves taken after ten hours exposure of mild steel in seawater without and with various concentrations of 2,4,6-triamino-3-pentadecylphenyl acetate at 30 °C and pH 8.

The values of the corrosion rate (C.R) in millimetres per year (mmpy) were calculated using Equation 1.

$$C.R \text{ (mmpy)} = \frac{315.36 i_{corr} \text{ (mm y}^{-1}) \times (E.W)}{\rho \times F}$$
 (1)

Where; *E.W* is the equivalent weight of iron (g); i_{corr} is the corrosion current density (μ A cm⁻²); ρ is the density of metal (g·cm⁻³) and *F* is the Faraday's constant (96500 C mol⁻¹). The

inhibition efficiency (*IE*) of the inhibitor was calculated using Equation (2).

$$IE(\%) = 100 \left(\frac{C.R_u - C.R_i}{C.R_u} \right) \tag{2}$$

Where; $C.R_u$ = Corrosion rate without inhibitor, $C.R_i$ = Corrosion rate with inhibitor.

Table 2: Electrochemical parameters obtained from polarization measurements on mild steel electrodes without and with various concentrations of 2,4,6-triamino-3-pentadecylphenyl acetate at 30 °C and pH 8

F -						
C_{inh}	b_a b_c		E_{corr}	i_{corr}	C.R	IE
(ppm)	(mV/dec)	(mV/dec)	(mV vs. Ag/AgCl)	$(\mu A cm^{-2})$	(mmpy)	(%)
0	16	-28	-728	9.395	1.089	_
100	20	-21	-722	1.306	0.151	86
200	19	-23	-719	0.958	0.111	90
300	19	-24	-685	0.694	0.080	93
400	20	-22	-675	0.692	0.080	93

It is observed from Table 2 that the C.R and i_{corr} decrease significantly with an increase in inhibitor concentrations, whereas E_{corr} shifts to the less negative value of potential as the

inhibitor concentration increases. The inhibition efficiency of 2,4,6-triamino-3-pentadecylphenyl acetate increased gradually as concentrations were increased. Furthermore,

Table 2 shows that the maximum inhibition efficiency of 93% was achieved using 300 ppm, which implies that 300 ppm is the minimum concentration of the inhibitor that gives optimum corrosion protection.

EIS measurements

The measurements were taken in seawater without and with various concentrations of 2,4,6-triamino-3-pentadecylphenyl acetate. The impedance spectra obtained in Nyquist format are shown in Figure 5.

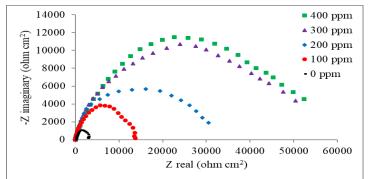


Figure 5: Impedance plots in Nyquist format taken after ten hours exposure of mild steel in seawater without and with various concentrations of 2,4,6-triamino-3-pentadecylphenyl acetate at 30 °C and pH 8.

Figure 5 shows that the impedance plots are characterized by depressed semicircles, whose sizes or diameters increased significantly as the 2,4,6-triamino-3concentrations of pentadecylphenyl acetate were increased. However, beyond 300 ppm of 2,4,6-triamino-3pentadecylphenyl acetate, the changes in the diameter of the semicircle are not significant. The equivalent circuit parameters, i.e., solution resistance (Rs), charge transfer resistance (Rp), phase and constant element (Q)dimensionless value (n) were obtained from the impedance plots using a complex non-linear least-square fitting programme, EQUIVCRT, developed by Boukamp. The readings were taken from the best-fit semicircle with $0.7 \le n$ ≤ 1 and the results obtained are summarized in Table 3. The values of corrosion current density (i_{corr} , μA cm⁻²) were calculated using the Stern-Geary equation (Equation (3). From the obtained values of corrosion current density (i_{corr}) , the values of corrosion rate (C.R) and inhibition efficiency (IE) were calculated using Equations 1 and 2, respectively.

$$i_{corr}(\mu A \text{ cm}^{-2}) = \frac{1}{2.303} (\frac{b_a b_c}{b_a + b_c}) \frac{1}{Rp}$$
 (3)

Where; Rp is the polarization resistance, b_a and b_c are anodic Tafel slope and cathodic Tafel slope, respectively. The values of the double-layer capacitance (Cdl) were calculated by using Equation 4.

$$Cdl = Q(Rs^{-1} + Rp^{-1})^{\frac{\mathbf{n} - 1}{\mathbf{n}}}$$
 (4)

As can be observed from Table 3, the values of open circuit potential become less negative as concentration of 2,4,6-triamino-3the pentadecylphenyl acetate increases. Whereas the values of solution resistance (Rs), charge transfer resistance (Rp)and inhibition efficiency (IE) increase significantly as the concentrations 2,4,6-triamino-3pentadecylphenyl acetate increase due to adsorption of the inhibitor molecules on the metal surface.

Table 3: Electrochemical parameters obtained from impedance measurements on mild steel electrodes without and with various concentrations of 2,4,6-triamino-3-pentadecylphenyl acetate at 30 °C and pH 8

r									
C_{inh}	E_{OCP}	R_S	R_p	n	Q	C_{dl}	i_{corr}	C.R	ΙE
(ppm)	(mV vs.	Ω	$(\Omega \text{ cm}^2)$		(μF	(μF	$(\mu A cm^{-2})$	(mmpy)	(%)
	Ag/AgCl)	cm ²)			cm ²)	cm ²)			
0	-734	38.58	2104	0.829	530	1121	2.101	2.440	_
100	-725	77.31	10006	0.711	164	956	0.445	0.515	79
200	-720	189.64	19149	0.727	103	738	0.236	0.273	89
300	-698	189.64	29574	0.716	65	520	0.156	0.181	93
400	-683	268.64	40114	0.719	56	497	0.113	0.131	95

As the inhibitor gets adsorbed on the metal surface, a protective film layer is formed on the metal surface creating a barrier against the release of electrons from the metal surface, hence the values of Rs, Rp and IE increase as the inhibitor concentrations increase. However, a decrease in the values of constant phase element (Q), double layer capacitance (Cdl), corrosion current density (i_{corr}) and corrosion rate (C.R) is observed as the concentrations of 2,4,6-triamino-3-pentadecylphenyl increase. When a metal is immersed in an aqueous solution, an electric double layer is formed at the metal interface between the positive charge on the metal surface and negative charge in the solution. Once the inhibitor is added to that aqueous solution, the inhibitor gets adsorbed on the metal surface forming a protective layer over the metal surface that acts as an insulator on the metal interface. This reduces the electrostatic attraction between the positive charge on the metal surface and negative charge in the solution; thus, the values of Cdl decrease as the inhibitor concentrations increase. Furthermore, it can also be observed that the optimum inhibition efficiency of 93% was achieved with 300 ppm of 2,4,6-triamino-3-pentadecylphenyl acetate, above which no significant increase in corrosion inhibition was recorded.

Adsorption isotherms analysis

The degree of metal surface coverage (θ) by the inhibitor molecules is dependent on the inhibitor concentration (C_{inh}) . The values of θ are derived from the values of inhibition

efficiency (IE) of the inhibitor, by assuming that the maximum value of IE is 100%. For example, if 200 ppm of the inhibitor exhibited the corrosion efficiency of 90%, then $\theta = 0.9$. If θ is a fraction of the metal surface covered by the inhibitor, then the fraction of the metal surface uncovered by the inhibitor is given by 1- θ . The obtained values of the degree of surface coverage from 100 to 400 ppm of the inhibitor were graphically fitted into various adsorption isotherms to find the best fit adsorption isotherm. Among the adsorption isotherms studied, Langmuir adsorption isotherm was found to give the best-fit for the adsorption of 2,4,6-triamino-3pentadecylphenyl acetate on the mild steel surface in seawater. The Langmuir adsorption isotherm was obtained by plotting the term $\log\left(\frac{\theta}{I-\theta}\right)$ as a function of the term $\log C_{inh}$ in Equation 5.

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + \log C_{inh} \tag{5}$$

Where; C_{inh} , θ and K are inhibitor concentration, fraction of the metal surface covered by the inhibitor derived from inhibitor efficiencies and equilibrium constant for the adsorption and desorption of the inhibitor, respectively. The Langmuir adsorption isotherm obtained from electrochemical impedance results is shown in Figure 6.

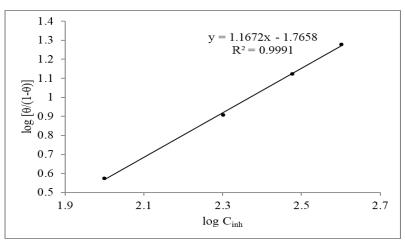


Figure 6: A plot of Langmuir adsorption isotherm for the mild steel immersed in inhibited seawater at 30 °C and pH 8 for the impedance data.

As expected, a plot of
$$\log \left(\frac{\theta}{1-\theta} \right)$$
 as a function

of $\log C_{inh}$ gave a straight line with a slope of 1.1672 and an intercept of -1.765. These results deviated slightly from an ideal Langmuir adsorption isotherm, suggesting that the adsorption mechanism of the 2,4,6-triamino-3-pentadecylphenyl acetate on mild steel to be chemical adsorption. Similar observations were previously reported in the work done by Kosari et al. (2014) and Larouj et al. (2015).

Conclusion

The optimum corrosion inhibition efficiency (93%) on mild steel exposed in seawater was achieved using 300 ppm of 2,4,6-triamino-3-pentadecylphenyl acetate. The results obtained from the two electrochemical techniques were found to be in good agreement. The polarization study indicates that 2,4,6-triamino-3-pentadecylphenyl acetate is a mixed type inhibitor with predominant anodic effect. The adsorption of 2,4,6-triamino-3-pentadecylphenyl acetate on mild steel surface obeyed the Langmuir adsorption isotherm which seems to be via chemical adsorption.

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Conflict of interest

The authors declare no conflict of interest regarding the publication of this paper.

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