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Research Article

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Inhibition of corrosion of aluminium in 1.0 M NaOH using 1-(2, 4-dihydroxyphenyl)-3-(2-hydroxyphenyl)-propenone

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ABSTRACT

The inhibitive effect of 1-(2,4-dihydroxyphenyl)-3-(2-hydroxyphenyl)-propenone on the corrosion of aluminium in 1.0 M NaOH was investigated by weight loss, potentiodynamic polarization and electrochemical impedence measurements. The inhibition efficiencies of this compound increase with increasing concentration. The results obtained from chemical and electro chemical techniques were in good agreement. The surface morphology of the metal surface was investigated by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) examination. The results revealed that the compound to appear inhibit corrosion through physisorption. Polarization measurements revealed that this compound act as a mixed type inhibitor.

Keywords: Aluminium; Inhibition; Adsorption; Polarisation; Impedance.

INTRODUCTION

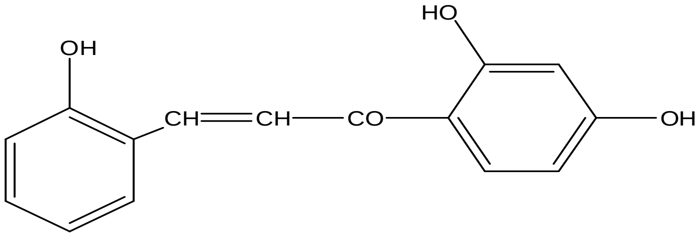
Aluminium ,being a metal with a high electronegative potential (-1.67 V_{SHE}) and high theoretical energy density (8.10Whg^{-1}) ,and therefore it is used in aluminum-air battery [1].Reports show that aluminium kept in alkaline medium and connected to an air electrode, produces high energy density and very high power [2,3]. Its production cost is low and there exists a large base for its manufacture and distribution [3]. Aluminium is highly resistant to most acidic and neutral solutions due to the formation of a protective oxide film on its surface [4]. Thus aluminium is considered a better anode for alkaline-air batteries amongst the available anodes. However its protective oxide film can be broken very quickly by the action of strong alkaline solutions, followed by substantial corrosion which induces coloumbic loss on discharge and fuel loss during standby. Therefore, for commercial applications of the alkaline aluminium air battery, it is necessary to add corrosion inhibitors either to the metal or to the electrolyte. The organic compounds containing heteroatoms like N, O, S and multiple bonds in their molecule are reported to be effective inhibitors for the corrosion of metals in different media [5 – 14]. The adsorption of inhibitors on metal surface is influenced by the surface charge of the metal and the chemical structure of organic inhibitors [15]. The aim of the study is to determine the inhibitive influence of, 1-(2, 4-dihydroxy phenyl)-3-(2-hydroxy phenyl) -propenone on the corrosion of aluminium in sodium hydroxide solution.

EXPERIMENTAL SECTION

Commercially pure aluminium samples, for the weight loss studies were cut into 2 cm x 1 cm x .14 cm coupons and polished with emery papers of different grades to mirror shine degreased with acetone, washed with double distilled water, and dried before immersing in the corrosion medium. The aluminium specimens for the electrochemical measurements were machine cut into test electrodes of dimension, 8 cm x1 cm x 0.14 cm and coated with epoxy resin (araldite) leaving a surface area of $1cm^2$. The corrosive medium, 1.0 M NaOH solution was prepared from analytical reagent grade NaOH (MERCK) and double distilled water.

Synthesis of 1- (2, 4-dihydroxy phenyl)-3-(2-hydroxy phenyl)-propenone (DPHPP)

The compound, 1- (2,4-dihydroxy phenyl)-3-(2-hydroxy phenyl)-propenone was synthesized and recrystallised as per the reported solvent-free synthesis procedure detailed below [16]. A mixture of O-hydroxybenzaldehyde (0.43 mol) and 2, 4-dihydroxyacetophenone (0.43 mol) and sodium hydroxide (0.55 mol) was ground by pestle and mortar at room temperature for 5 minutes. The precipitated product was purified by hot ethanol and was identified by U.V and I.R spectra. The molecular weight of the compound is 256. The structure of the molecule is shown below. The DPHPP was dissolved in 1.0 M sodium hydroxide in appropriate quantities for the inhibition studies.



Weight loss measurements

The aluminium specimens prepared for the study as described above were weighed and suspended in beakers containing 100 ml of aerated unstirred 1.0 M NaOH solutions without and with the inhibitor for stipulated period of time, with the aid of glass hooks. To determine the weight loss the coupons were retrieved after one hour, scrubbed with bristle brush under running water until they are clean, dried in acetone and re-weighed.

Electrochemical measurements

The aluminium coupons which were prepared as described above were used as working electrode. Before each experiment, the exposed area of the working electrode was polished with soft 3M 1500 sand paper, to a metallic shine. Then it was washed with distilled water, degreased with ethanol, and finally dried with soft paper. The electrochemical measurements were performed in a conventional three electrode glass cell which consists aluminium as working electrode (WE), platinum counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. The electrode potential was allowed to stabilize 60 min before starting the measurements. Measurements were performed using Princeton Applied Research Electrochemical Analyser (model K0264 Micro cell kit). Electrochemical analyser software was used for plotting, graphing and fitting data. Tafel polarization curves were obtained by changing the electrode potential automatically from -1.7 mV to -1.1 mV around open circuit potential with scan rate of 10 mV/sec. Impedance measurements were carried out in frequency range from 100 kHz to 10 Hz using ac signals with an amplitude of 27 mV peak to peak at open circuit potential.

SEM and EDX analysis

SEM and EDX analysis was performed using JEOL MODEL-JSM 6390 made in Japan. Prior to analysis, the Al specimens were kept immersed in 1.0 M NaOH for 1 hr in the absence and presence of 2.5x10^{-3}, 1-(2,4-dihydroxy phenyl)-3-(2-hydroxy phenyl)-propenone..Finally, the specimens were washed thoroughly to remove loosely adsorbed ions.

RESULTS AND DISCUSSION

3.1. Weight loss measurements

The percentage inhibition efficiency was calculated using the equation [17].

$$\text{Percentage inhibition} = \frac{W_0 - W_i}{W_0} \times 100 \qquad (1)$$

Where, W_0 and W_i are the weight losses in the absence and in the presence of the inhibitor respectively. The percentage inhibition efficiency values, obtained from weight loss data, are summarized (Table1).

Table 1 Inhibition of corrosion of aluminium in 1.0 M NaOH by DPHPP at $30 \pm 0.5\,°C$

Concentration	$\frac{W_0 - W_i}{W_0}$	%IE
1.00 x 10^{-5}	0.111	11.1
2.50 x 10^{-5}	0.133	13.3
1.00 x 10^{-4}	0.244	24.4
2.50 x 10^{-4}	0.377	37.7
1.00 x 10^{-3}	0.660	66.0
2.50 x 10^{-3}	0.822	82.2

A maximum of 82.2 % corrosion inhibition is observed at 30 $°C$. The degree of surface coverage θ for the different concentrations of this DPHPP, has been evaluated from the weight loss measurements. The data were fitted to the adsorption isotherm such as El-Awadys et al, Langmuir, Flory-Huggins, Temkin and Frumkin Isotherms.The regression coffecient R^2 was used to determine the best fit isotherm [18]. It was found that R^2 = =0.988 for Langmuir isotherm.

Langmuir adsorption isotherm model has the form,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + c \qquad (2)$$

where θ is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process Fig.1 Plot of C/θ versus C is shown.

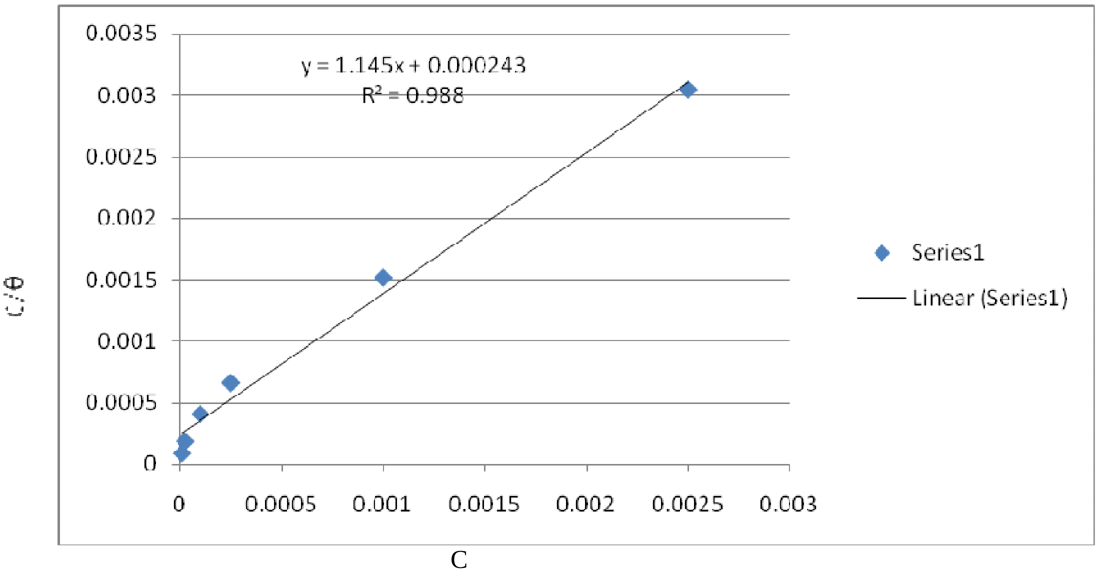


Figure 1.

The slope deviates from unity indicating that there is attraction or repulsion in the adsorbed layer of inhibitor on the aluminium surface. [19, 20].

Using Langmuir adsorption isotherm, $K_{ads} = \frac{\theta}{C(1-\theta)}$, K_{ads} values are calculated at different concentrations of the inhibitor. The values of K_{ads} are related to the standard Gibbs free energy of adsorption $\Delta G^{\circ}{}_{ads}$ by the following equation.

$$K_{ads} = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G^{\circ}{}_{ads}}{RT}\right) \qquad \text{……….. (3)}$$

$C_{solvent} = C_{H_2O}$ = 55.55 moldm^{-3} , R (J mol^{-1} K^{-1} is the gas constant and T (K) is the temperature.

The standard Gibbs free energy of adsorption of DPHPP on the aluminium surface at 303K was calculated (Table 2).

Table 2

Concentrations	θ	$\Delta G^{\circ}{}_{ads}$, kJ mol^{-1}
1.00 x 10^{-5}	0.111	-33.881
2.50 x 10^{-5}	0.133	-32.056
1.00 x 10^{-4}	0.244	-30.462
2.50 x 10^{-4}	0.377	-29.730
1.00 x 10^{-3}	0.660	-29.194
2.50 x 10^{-3}	0.822	-29.069

The values of $\Delta G^{\circ}{}_{ads}$ are negative and lies between -33.881 and -29.069 kJmol^{-1}. The negative value indicates that the adsorption of the inhibitor molecule on the aluminium surface is spontaneous. The values are less negative with an increase in inhibitor concentrations, indicating that the adsorption of the inhibitor onto aluminium surface was less favourable with increasing concentrations of the inhibitor.

In general, the values of $\Delta G^{\circ}{}_{ads}$ around -20 kJ mol^{-1} are consistent with physisorption while those around -40 kJ mol^{-1} or higher correspond to chemisorptions [21, 22].

3.2 Potentiodynamic polarization measurements

The polarization behaviour of aluminium electrode in 1.0 M NaOH solutions in the absence and presence of different concentrations of DPHPP at a scan rate of 10 mV/sec is shown. (Fig.2).

The cathodic and anodic branches of the polarization curves are shifted from the corrosion potential(E_{corr}) slightly in the positive direction and both the anodic and cathodic current densities are reduced with the increase of inhibitor concentration. The anodic current was reduced more significantly than the cathodic current. These results indicate that the corrosion process is under anodic control and the inhibitor acts as of mixed type [3]. The corrosion potential(E_{corr}), corrosion current density (i_{corr}), anodic and cathodic slopes (β_a andβ_c) at different inhibitor concentrations are shown (Table 3).

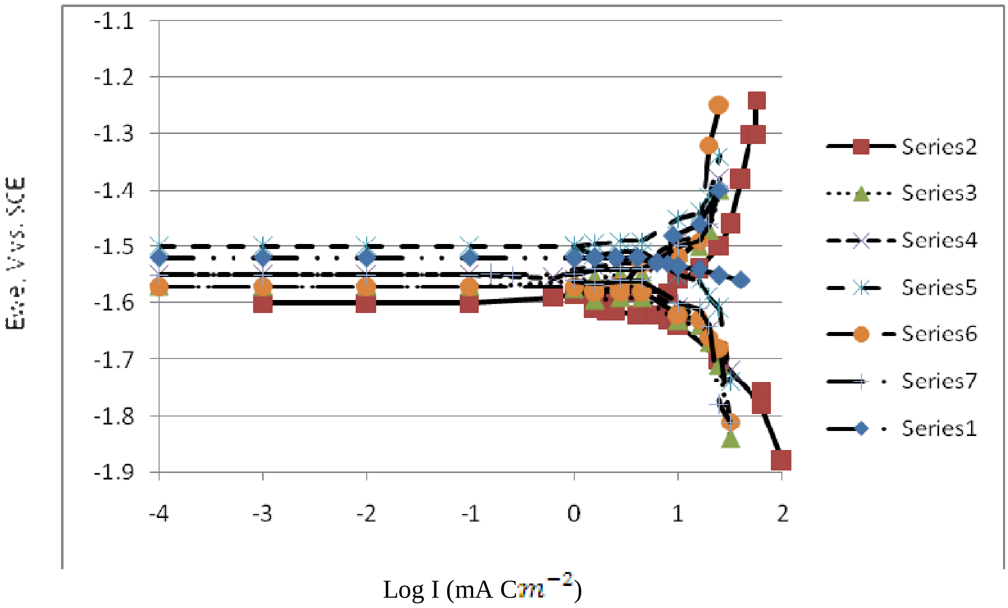


Figure 2 {series2=blank, series3=1X10^{-5}, $series4 = 2.5X10^{-5}, series\ 5 = 1.00X10^{-4}$, series6=2.5X$10^{-4}$, series 7=1.00X$10^{-3}$, series1 = 2.50X$10^{-3}$ }

Table 3: The electrochemical parameters (i_{corr}, E_{corr}, β_a and β_c) obtained from potentio-dynamic polarization of Al in 1.0 M NaOH in the absence and in the presence of different concentrations of inhibitor at $30 \pm 0.5°C$.

[Concentration], M	E_{corr}, V	I_{corr}, mA cm^{-2}	β_c, mV dec^{-1}	β_a, mV dec^{-1}
Blank	-1.592	16.135	270.5	496.5
1.00 x 10^{-5}	-1.575	13.911	212.4	527.7
2.50 x 10^{-5}	-1.549	11.789	220.5	574.0
1.00 x 10^{-4}	-1.494	10.370	207.7	396.3
2.50 x 10^{-4}	-1.572	9.915	189.0	457.0
1.00 x 10^{-3}	-1.544	7.914	211.1	540.7
2.50 x 10^{-3}	-1.480	8.606	189.3	303.5

According to Ferreira et al. [23, 24] and Li et al. [23, 24] if the displacement in corrosion potential is more than $\pm 85\ mV$, with respect to corrosion potential of the blank, the inhibitor can be considered as a cathodic or an anodic type. However, the maximum displacement in this study is +112 mV indicating that the inhibitor inhibits predominantly anodic reaction.

3.3. Impedence measurements

The influence of different concentration DPHPP on the impedence response of Al in 1.0 M NaOH solution at ocp and at $30 \pm 0.5°C$ is shown (Fig.3).

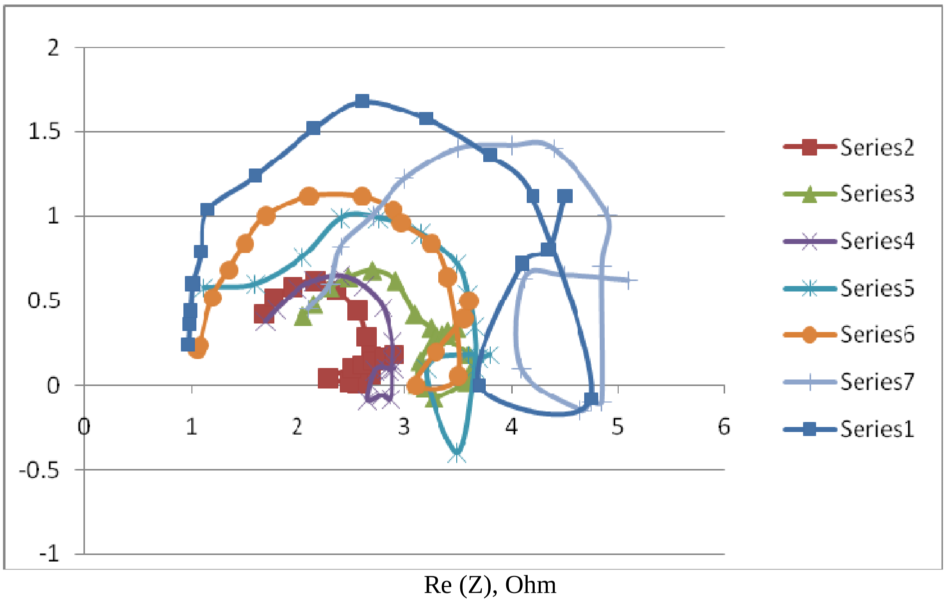


Figure 3 {series2=blank, series3=1X10^{-5}, $series4 = 2.5X10^{-5}$, $series\ 5 = 1.00X10^{-4}$, series6=2.5X10^{-4}, series 7=1.00X10^{-3}, series1 = 2.50X10^{-3} }

The impedence diagram consists of a large capacitive loop at high frequencies (HF), and a small inductive one at medium frequencies (MF). The HF capacitive loop could be assigned to the relaxation process in the aluminium oxide film present on the aluminium surface and its dielectric properties [25,26]. The electrode impedence in the oxide which is considered a parallel circuit of a resistor due to the ionic conduction in the oxide film, and a capacitor due to its dielectric properties [26] was determined by the metal/oxide interface, the oxide film, and the oxide/solution interface. The inductive loop observed at MF may be attributed to the relaxation process in oxide layer, containing adsorbed species such as OH^{-}_{ads} [27]. The values of the polarization resistance (R_p) and the double layer capacitance (C_{dl}) were recorded (Table 4). The (R_p) value increases and (C_{dl}) value decreases with increase in inhibitor concentration, due to the adsorption of the inhibitor on the electrode surface [28, 29].

Table 4. Values of R_p and C_{dl} for Al in 1.0 M NaOH solution in the absence and presence of various concentrations of the inhibitor at ocp and at $30 \pm 0.5°C$.

[Inhibitor], M	R_p, ohm	$C_{dl}, \mu F$
Blank	0.9075	55.5
1.00 x 10^{-5}	1.009	73.25
2.50 x 10^{-5}	1.554	69.8
1.00 x 10^{-4}	1.555	47.52
2.50 x 10^{-4}	2.3	0.00148 6
1.00 x 10^{-3}	2.4	--
2.50 x 10^{-3}	3.082	0.00163 7

4. 1 Scanning electron microscopy [30, 31]

For surface morphology study, SEM analysis was carried out on the Al samples immersed in 1.0 M NaOH solution for 1hr in the presence and absence of the inhibitors. The SEM images of the bare aluminium surface and aluminium surface in 1.0 M NaOH are displayed (Fig 4a and 4b). The fig.4c shows that DPHPP almost completely covers the material surface and protects it from the aggressive media.

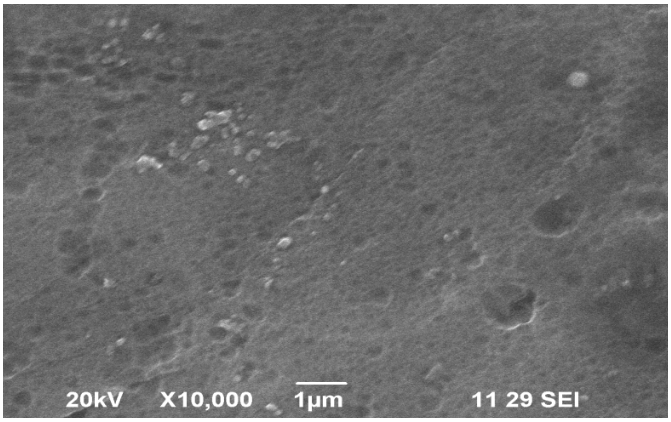


Fig.4a

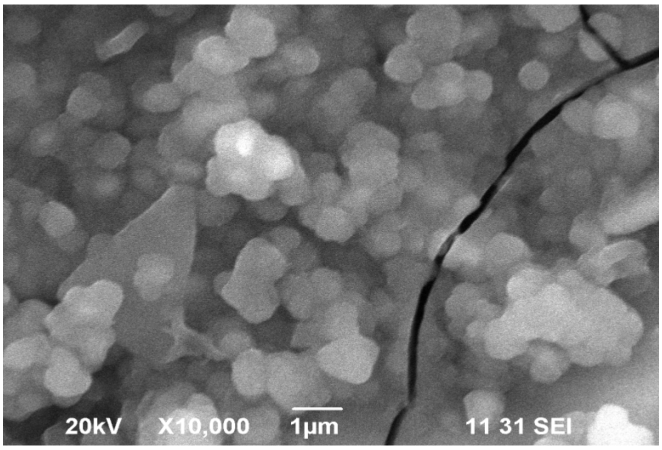


Fig.4b

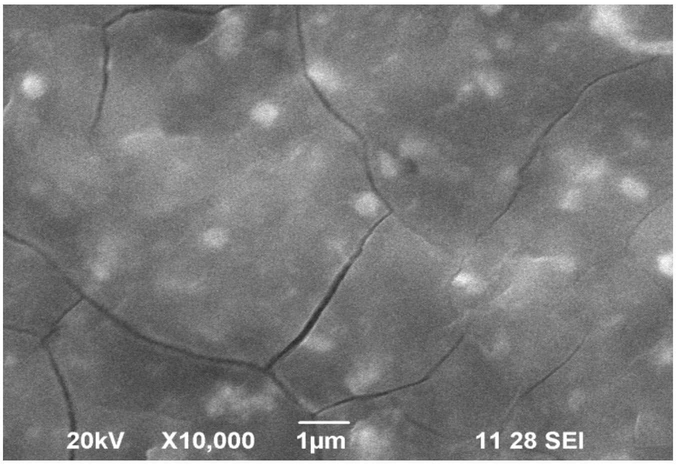


Fig.4c

The formation of adsorbed film on Al surface was confirmed by EDX examinations of the metal surface.

4.2. EDX examinations of the electrode surface [1].

EDX survey spectra were used to determine which elements were present on the Al surface before and after exposure to the inhibitor solution. The surface film composition after aluminium has been immersed for 1 hr in 1.0 M NaOH solution in the absence and presence of 2.50 x $10^{-3}M$ of the inhibitor was determined by EDX survey spectra .Fig.5a,-EDX spectra for the bare aluminium surface. The metal surface in the absence of inhibitor shows only aluminium and oxygen with a ratio of about 2:3 indicating that the metal surface contained only Al_2O_3 film (Fig.5b).

Fig5. EDX spectra recorded for Al specimen immersed for 1hr in sodium hydroxide (1.0 M) solution in the presence of 2.5 x 10^{-3}M of DPHPP at $30\pm0.5°C$.

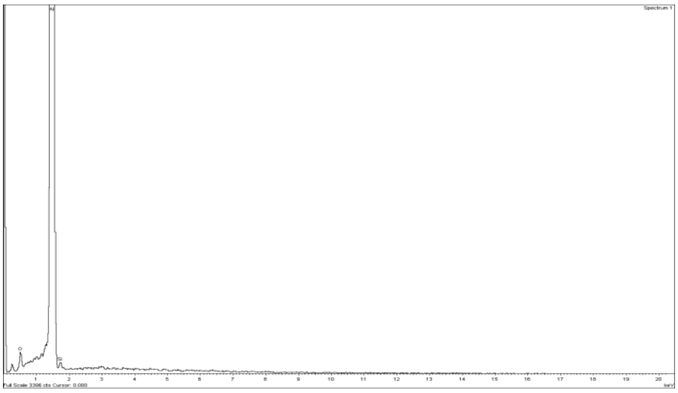


Fig. 5a

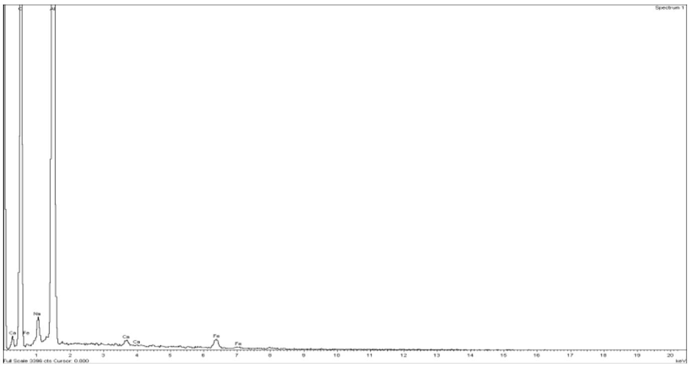


Fig.5b

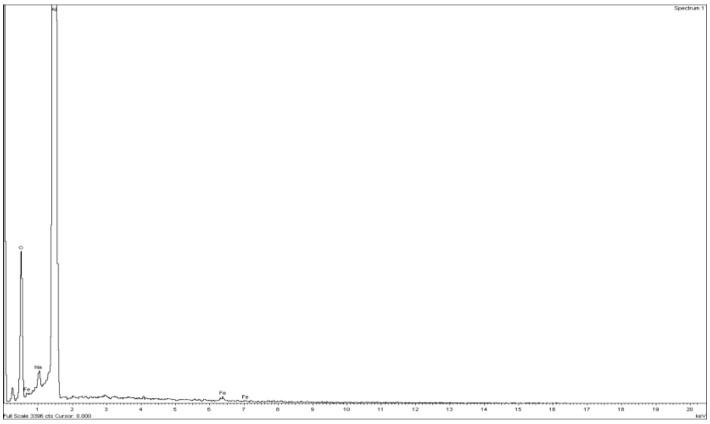


Fig.5c

The metal surface in the presence of inhibitor shows only aluminium and oxygen with a ratio of about 3:1 indicating that the aluminium corrosion controlled by the inhibitor (Fig.5c).

CONCLUSION

- The inhibition efficiency of 1-(2, 4-dihydroxy phenyl)-3-(2-hydroxy phenyl)-propenone increases with the increase in inhibitor concentration.
- The inhibitor behaves as a mixed type inhibitor, predominantly affecting the anodic reactions.
- The inhibitor, 1-(2, 4-dihydroxy phenyl)-3-(2-hydroxy phenyl)-propenone attach on to the aluminium surface through physisorption and obeys Langmuir's adsorption isotherm model.
- The inhibition efficiency obtained from potentiodynamic polarization method and EIS technique are in reasonably good agreement.

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