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Inhibition effect of 4-(2-hydroxyphenyl)-but-3-en-2-one on the corrosion of aluminium in NaOH solution

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ABSTRACT

The corrosion inhibition properties of 4-(2-hydroxyphenyl)-but-3-en-2-one (HPB) in 1M NaOH solutions were studied using chemical and electrochemical techniques. The inhibition efficiency was found to increase with increasing concentration and decrease with increasing temperature. The corrosion inhibition data have been analyzed using different isotherms like Langmuir, Temkin and El-Awady's isotherms. Polarisation curves reveal that HBP act as the mixed type inhibitor. Electrochemical impedance exhibits a large capacitive loop at high frequencies followed by an inductive loop at medium frequencies. The surface morphology of aluminium in the presence and absence of inhibitor was studied by using SEM images.

Keywords: Aluminium corrosion, inhibition, adsorption isotherm and electrochemical methods.

INTRODUCTION

Aluminium lends wide range of industrial applications especially in aerospace, household industries and commonly used in marine applications. This is because of the combination of light weight, good appearance and mechanical strength, high thermal and electrical conductivity. In addition they are applied as the materials for body panels of the automobile and the hydrogen gas vessels with high temperature applications[1-3]. The low atomic mass of aluminium and its ability to transfer of three electrons per atom, complied with the negative value of the standard electrode potential make the metal potentially attractive as an anode material for power sources with high energy densities[4]. Aluminium depends on the presence of natural surface oxide film for its high corrosion resistance in several media, but alkaline solutions are known to render the oxide film non-protective, because OH^- ion dissolves the protective oxide and the aluminium surface establishes a very negative potential, with the formation of aluminates ion[5-11]. This wasteful self-corrosion results in inacceptable high energy loss during standby and the safe problem for the use of batteries. Minimize the self corrosion by modify the electrolyte with the addition of organic inhibitors[12-16]. Many researches showed that the electrochemical behaviours of aluminium largely depend on the applied electrolyte[17,18]. Successful inhibitors should keep aluminium anode electrochemically active while reducing its corrosion rate to a low level. Several workers have employed organic and inorganic compounds as corrosion inhibitors to control this oxide film dissolution[19-22]. compared with Inorganic corrosion inhibitors, using organic corrosion inhibitors is an effective, inexpensive and less pollution means of reducing the degradation of metals[23-27]. Organic compounds containing polar groups such as N, S and O as well as aromatic

compounds with conjugated double bonds have been reported as good corrosion resistant for Aluminium in alkaline medium[28,29]. Due to the presence of the - C=C-group and O atoms in the HPB molecule, leads to be a good corrosion inhibitor.

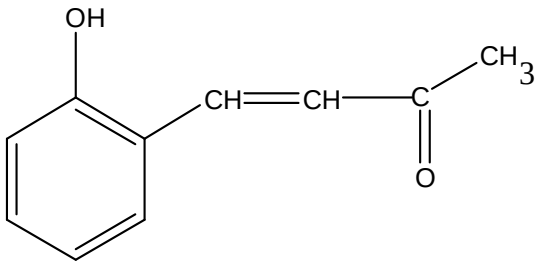
MATERIALS AND METHODS

2. Experimental

Commercially pure aluminium samples, for the weight loss studies were cut to form different coupons dimension, 2 cm x 1 cm x .14 cm. Each coupon was washed with ethanol, rinsed with acetone and allowed to dry in the air and preserved in desiccators. 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.

2.1. Synthesis of 4-(2-hydroxyphenyl)-3-butene-2-one.

The compound, 4-(2-hydroxyphenyl)-3-butene-2-one was synthesized and recrystallised as per the reported synthesis procedure detailed below[30]. A mixture of O-hydroxybenzaldehyde (0.43 mol) and acetone (0.43 mol) and sodium hydroxide (0.55 mol) was stirred continuously with mechanical stirrer at room temperature for 2-3 hours. The reaction mixture is left overnight in a refrigerator. The separated product was filtered on a Buchner funnel and washed with cold water. 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 162. The structure of the molecule is shown below. The HPB was dissolved in 1.0 M sodium hydroxide in appropriate quantities for the inhibition studies.



2.2. Weight loss measurements

The known weight of aluminium specimen was immersed in beakers containing 100 ml of aerated unstirred 1.0 M NaOH solutions without and with the inhibitor, with the aid of glass hooks. To determine the weight loss the coupons were withdrawn from the test solution after one hour, scrubbed with bristle brush under running water until they are clean, dried in acetone and re-weighed.

2.3. 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 Analyzer (model K0264 Micro cell kit). Electrochemical analyzer 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 amplitude of 27 mV peak to peak at open circuit potential.

2.4. SEM analysis

SEM 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 0.01, 4-(2-hydroxyphenyl)-3-butene-2-one. Finally, the specimens were washed thoroughly to remove loosely adsorbed ions.

RESULTS AND DISCUSSION

3.1. Weight loss studies

The values of inhibition efficiency obtained from weight loss experiment for corrosion of aluminium in 1.0M NaOH in presence of different concentration of HPB at 30°C and 50°C are given (Table1). The %IE was calculated from following relationship.

$$\%IE = \frac{W^{\circ}-W}{W^{\circ}} \times 100$$

Where, W^{o} and W are weight loss of aluminium in absence and presence of inhibitor.

Table -1. Calculation of Inhibition efficiency by using weight loss studies.

[Inhibitor] M	θ		%IE	
	30°C	50°C	30°C	50°C
0.000100	0.250	-	25	-
0.000250	0.318	-	31.8	-
0.000500	0.340	-	34.0	-
0.000750	0.431	-	43.1	-
0.001000	0.500	0.320	50.0	32.0
0.001250	0.523	0.328	52.3	32.8
0.002500	0.660	0.344	66.0	34.4
0.005000	0.705	0.496	70.5	49.6
0.007500	0.727	0.648	72.7	64.8
0.010000	0.750	-	75.0	-
0.012500	0.773	-	77.3	-

This suggests magnitude of adsorption and surface coverage by inhibitor on Aluminium surface increases with concentration of inhibitor[31-32].

3.2. Adsorption isotherm and thermodynamic parameters

The action of an inhibitor in aggressive alkaline media is assumed to be due to its adsorption at the metal/solution interface. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitor must be calculated. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitors in alkaline media have been evaluated from the weight loss studies and listed (Table-1). Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin and El-Awadys et al.

The Langmuir isotherm is given by[33].

$$\frac{\theta}{(1-\theta)} = k[c]$$

Where K is the binding constant representing the interaction of the inhibitor with the metal surface and C is the concentration of the inhibitor.

The El-Awady's et al isotherm is given by[34].

$$\log \left[\frac{\theta}{(1-\theta)}\right] = \log k' + y \log C$$

where y is the number of inhibitor molecules occupying one active site. The binding constant K is given by:

$$K = k'^{(1/y)}$$

It is important to note that values of 1/y less than unity imply the formation of multilayers of the inhibitors on the surface of the metal values of 1/y greater than unity, mean that a given inhibitor molecule will occupy more than one active site.

The Temkin isotherm is given by[35].

exp (-2aθ) = KC

Where K is the adsorption equilibrium and a is the interaction parameter if the interaction parameter values were negative, it reflects the repulsion exists in the adsorption layer. This result is coinciding with Langmuir adsorption. The slope deviates from unity indicating that there is attraction or repulsion in the adsorbed layer of inhibitor on the aluminium surface [36,37]. Fig 1-4 shows the adsorption of HPB to the Langmuir, El-awady's et al and Temkins isotherm model respectively. The parameters obtained from these figures are given (Table 2).

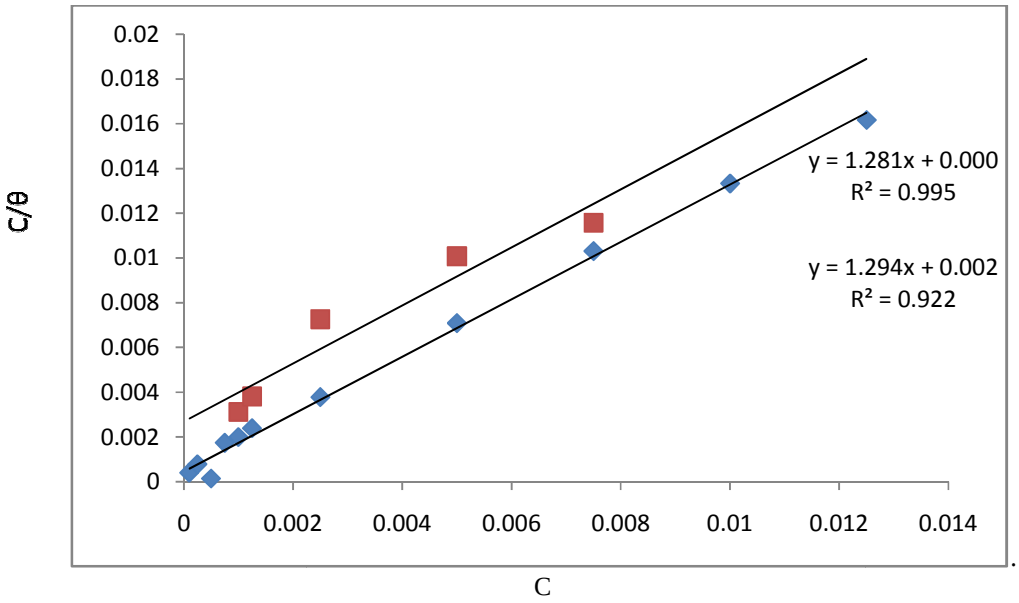


Fig.1. Langmuir's isotherm for the adsorption of HPB on the aluminium surface.

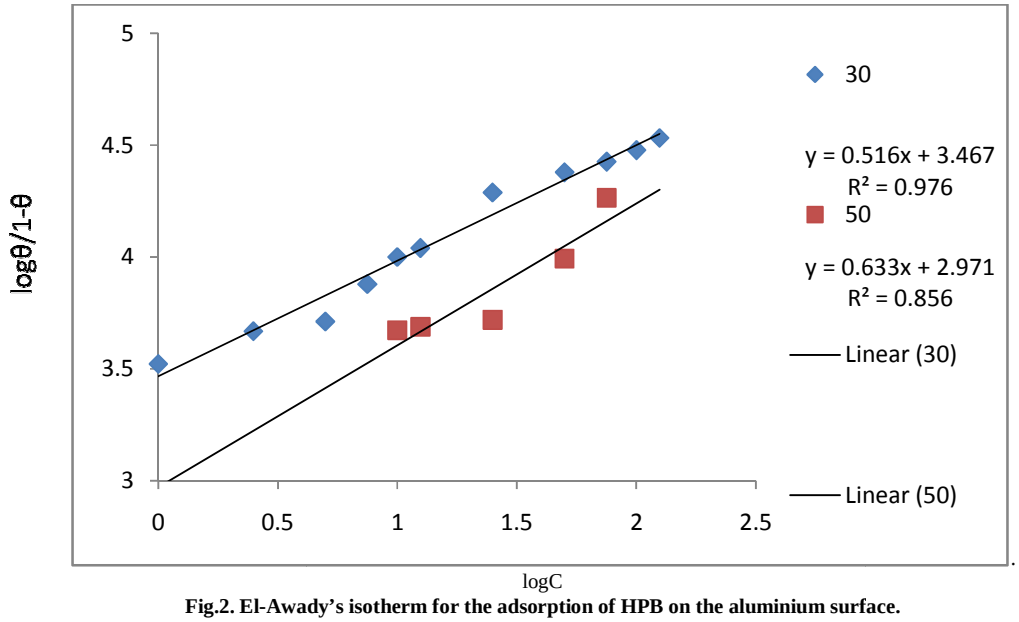


Fig.2. El-Awady's isotherm for the adsorption of HPB on the aluminium surface.

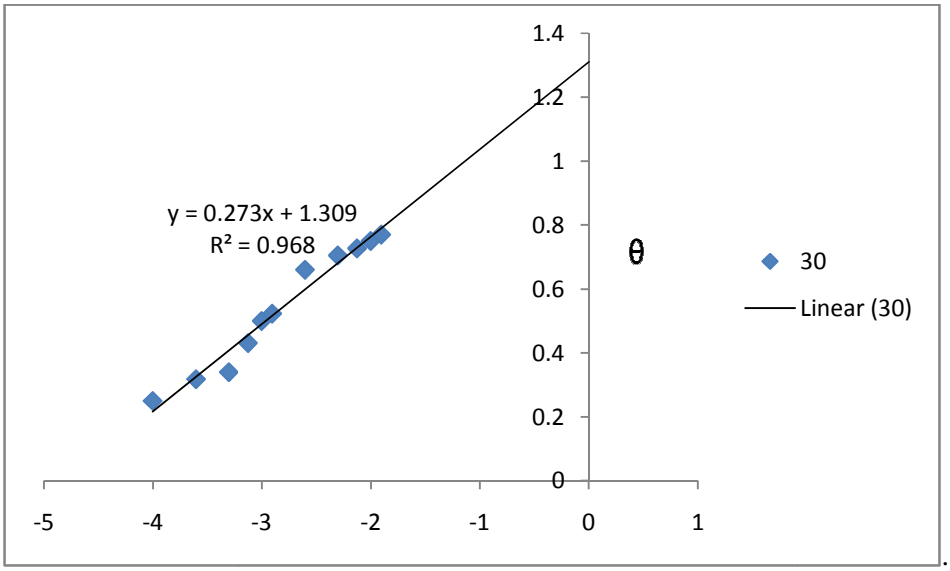


Fig.3.Temkin's isotherm for the adsorption of HPB on the aluminium surface at 30±0..5

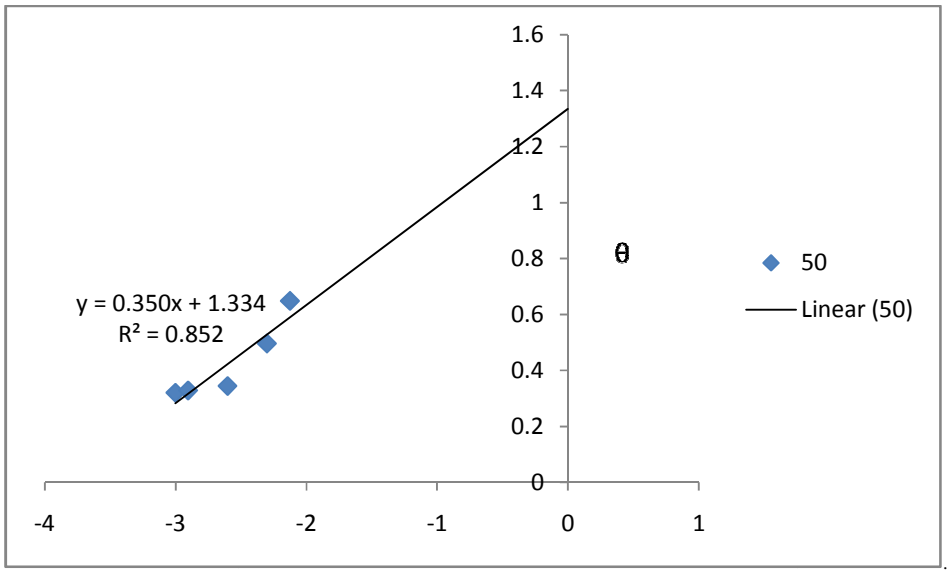


Fig.4. Temkin's isotherm for the adsorption of HPB on the aluminium surface at 50±0..5℃.

Table 2. Various parameters obtained from the adsorption isotherms.

Temperature	Langmuir		Temkins			El-awady's et all		
	R^2	$\Delta G°_{ads}$	R^2	$\Delta G°_{ads}$	a	R^2	$\Delta G°_{ads}$	1/y
30℃	0.995	-29.440	0.968	-37.907	-4.205	0.976	-49.139	1.94
50℃	0.922	-25.017	0.852	-32.183	-3.282	0.856	-37.356	1.58

The regression coefficient R^2 was used to determine the best fit isotherm[38].Among these three, the best fit was obtained(R^2 = 0.995) with the Langmuir adsorption .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 $\Delta G°_{ads}$ by the following equation.

$\Delta G°_{ads}$ = -2.303 RT log (55.5K_{ads})

where, ΔG°_{ads} is Gibbs free energy of adsorption, T is the temperature in Kelvin and K_{ads} is the equilibrium constant for the adsorption process and 55.5 is the molar concentration of water in solution. The standard Gibbs free energy of adsorption of HPB on the aluminium surface of different concentrations at 303K and 323K was calculated (Table 3). The spontaneity of the adsorption process and the stability of the adsorbed species on the aluminium surface were confirmed by the negative values of ΔG°_{ads} [39,40]. In general, the values of ΔG°_{ads} around -20 kJ mol^{-1} are consistent with physisorption while those around -40 kJ mol^{-1} or higher corresponds to chemisorptions[41,42]. The enthalpy of adsorption ΔH^{o}_{ads} and entropy of adsorption ΔS°_{ads} can also be calculated using the following basic thermodynamic equations and the values are listed (Table 3).

$$\frac{\Delta G^{o} ads}{T_1} - \frac{\Delta G^{o} ads}{T_2} = \Delta H^{o}_{ads} \frac{T_2 - T_1}{T_1 T_2}$$

$$\Delta G^{\circ}_{ads} - \Delta H^{o}_{ads} = T\Delta S^{\circ}_{ads}$$

The negative values of ΔH^{o}_{ads} inferred that the adsorption of inhibitor is an exothermic process[43].In an exothermic process, physisorption is distinguished from chemisorptions by considering the absolute value of adsorption enthalpy. As per the literature, the enthalpy of a physisorption process is lower than -41.86 kJ mol^{-1}while the enthalpy of a chemisorptions approaches -100 kJ mol^{-1} [43]. The calculated values of ΔH^{o}_{ads} obtained in this study are less than -41.86 kJ mol^{-1} indicates physical adsorption of HPB on the aluminium surface. The negative values of ΔS°_{ads} reveal that there is a decrease in disorderliness of the inhibitors on the aluminium surface[44].

Table 3. Various thermodynamic parameters for the adsorption of HPB on aluminium surface.

[inhibitor] M	ΔG°_1 kJ mol^{-1}	ΔG°_2 kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° J $mol^{-1}K$
0.00100	-27.523	-27.316	-30.630	-10.259
0.00125	-27.194	-26.815	-32.978	-19.088
0.00250	-26.886	-25.146	-53.235	-86.97
0.00500	-25.664	-24.975	-36.110	-34.5
0.00750	-24.915	-25.568	-24.024	-2.95

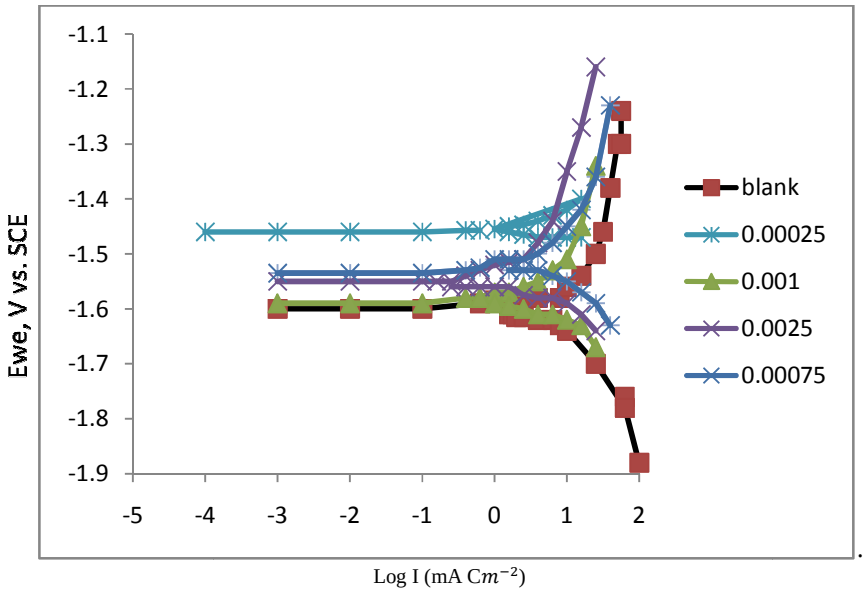


Fig .5. Potentiodynamic polarization curves for aluminium in 1M NaOH containing different concentrations of HPB.

3.3Polarisation curve measurements

To determine the polarization characteristics, a correct scan rate to be fixed. In this experiment 10 mV min^{-1} has been fixed as the proper scanning rate to evaluate the corrosion behaviour of aluminium in NaOH solution. Fig.5

displays the potentiodynamic polarization curves for aluminium in 1M NaOH solution containing different concentrations of HPB. The parameters include the corrosion potential, E_{corr}; anodic and cathodic Tafel constants, β_a and β_c; and the corrosion current density, i_{corr} are presented (Table4) .

Table 4. The electrochemical parameter for aluminium in alkaline solution containing different concentrations of HPB.

[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
2.50 x 10^{-4}	-1.422	13.836	251.6	401.5
7.50 x 10^{-4}	-1.569	11.626	202.0	506.4
1.00 x 10^{-3}	-1.591	9.016	191.2	480.4
2.50 x 10^{-3}	-1.518	6.510	206.1	479.4

It is observed that, the HPB affects both anodic and cathodic part of the polarization curves. This means that the HPB influence both the dissolution of aluminium and the hydrogen evolution processes indicating that the HPB behaves as mixed type inhibitor. The corrosion of aluminium occurs through an oxide film followed by dissolution at the oxide/electrolyte surface[45]. As indicated in table, increasing concentration of HPB increases the percentage of inhibition. This could be attributed to adsorption of the HPB on the anodic and cathodic sites of aluminium surface leading to decrease of the exposed area necessary for aluminium dissolution and hydrogen evolution[46,47].

3.4 Electrochemical impedance spectroscopy

Fig 6. represents the Nyquist diagram for aluminium in 1.0M NaOH at 30℃ without and with various concentrations of HPB. The impedence spectra consist of a large capacitive loop at high frequency (HF) followed by a small inductive loop one at low frequency.The values of the polarization resistance and double layer capacitance were recorded (Table 5).

Table 5. Impedance parameters for the corrosion of aluminium in 1M NaOH in the absence and presence of different concentration of HPB.

[Inhibitor], M	R_p, ohm	$C_{dl}, \mu F$
Blank	0.9075	55.5
2.50 x 10^{-4}	1.917	82.9
7.50 x 10^{-4}	1.424	51.89
1.00 x 10^{-3}	1.843	40.09
2.50 x 10^{-3}	2.989	53.16

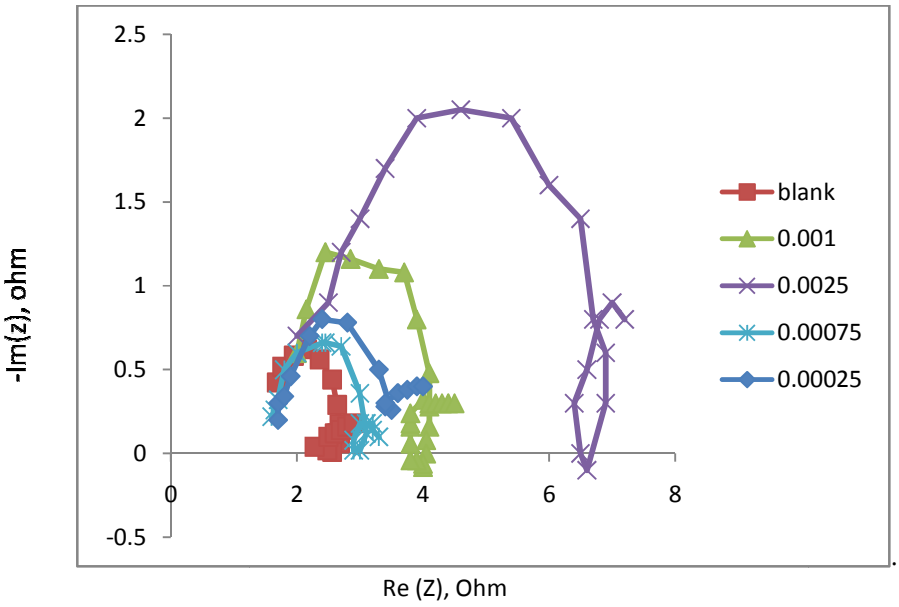


Fig .6. Nyquist plots for aluminium in the absence and presence of different concentrations of HPB.

After adding HPB the shape is not changed throughout a series of inhibitor concentrations, indicating that there is almost no change in the corrosion mechanism occurs due to the inhibitor addition. The capacitive loop at the HF is corresponding to the interfacial reactions; particularly the reaction of aluminium oxidation at the metal/oxide/electrolyte surface[48].The inductive loop arises due to the relaxation of adsorbed charged intermediates[49]. These high frequency loops are not perfect semicircles which can be attributed to the frequency dispersion as a result of the roughness and inhomogeneous of electrode surface[50].

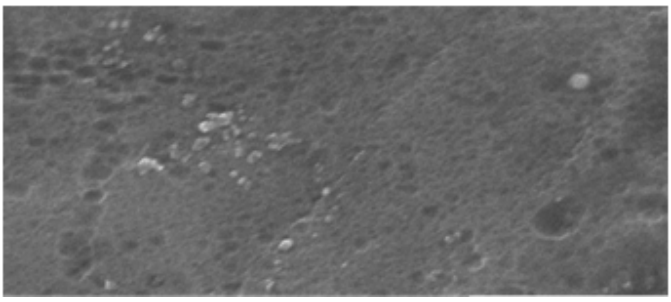


Fig.7a.

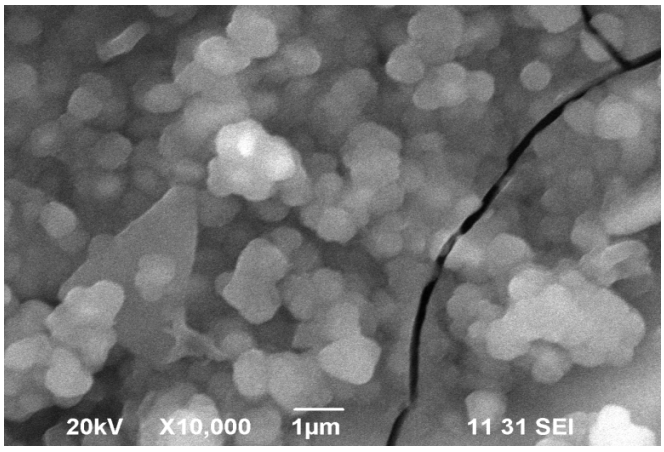


Fig. 7b.

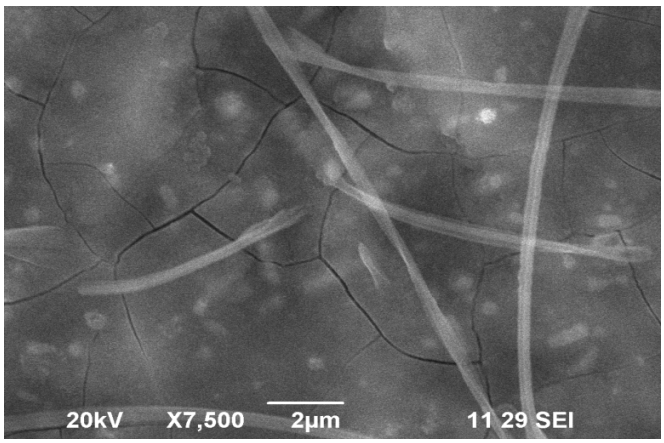


Fig.7c.

Scanning electron microscopy[51]

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 aluminium bare metal surface and without inhibitor in 1.0 M NaOH are displayed (Fig 7a and 7b).The fig 7b. displayed the pits and crevices on the metal surface. The fig.7c shows that HPB almost completely covers the material surface and protects it from the aggressive media.

CONCLUSION

1. 4-(2-hydroxyphenyl)-but-3-en-2-one acted as a good inhibitor for the corrosion of aluminium in 1M NaOH solution.
2. The percentage inhibition increases with the increase in inhibitor concentration and decreases with increase in temperature.
3. The adsorption of the inhibitor molecules on the aluminium surface obeys Langmuir adsorption isotherm.
4. Thermodynamic parameters indicated that the adsorption is spontaneous and exothermic process.
5. The inhibition efficiency obtained from chemical method and electrochemical method are in good agreement.

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