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The inhibition effect of [1-(2, 4-dihydroxy-Phenyl)-3-(4-hydroxy-3-methoxy-phenyl)-propenone] on the corrosion of the Aluminium in alkaline medium

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ABSTRACT

The adsorption characteristics of [1-(2,4-dihydroxy– phenyl)-3-(4-hydroxy- 3-methoxy-phenyl)- propenone (DPHMPP) on the corrosion of aluminium in alkaline medium was investigated at 30°C and 50°C by weight loss and polarization measurements. The inhibition efficiency was found to increase with increasing concentration of the inhibitor. The temperature studies showed a decrease in efficiency with rise in temperature. Synergistic effect of tetrabutylammonium bromide (TBAB) increased the inhibition efficiency of DPHMPP. Gasometric measurements showed that the addition of DPHMPP to NaOH suppressed the evolution of hydrogen gas. The inhibitor was found influence both the anodic and cathodic corrosion reactions and thus acts as mixed type inhibitor. The adsorption of the inhibitor was found to obey Langmuir, El-Awady, Temkins and Flory Huggins adsorption isotherms.

Keywords: Adsorption isotherm, Aluminium corrosion, chemical method, electrochemical method, organic inhibitor,

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INTRODUCTION

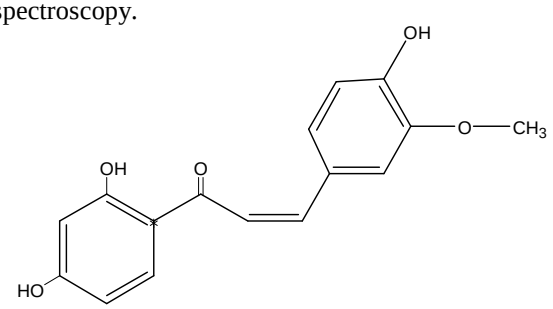
Aluminium is remarkable for its low cost, high strength to weight ratio and for its ability to resist corrosion. Structural components made from aluminium and its alloys are vital to the aerospace industry and are important in other areas of transportation and structural materials. Aluminium has excellent corrosion resistance due to a thin surface layer of aluminium oxide that forms when the metal is exposed to air, effectively preventing further oxidation. This corrosion resistance is greatly reduced by alkaline medium. Therefore the study of corrosion inhibition of aluminium in alkaline medium has gained great importance in recent years [1-3].

The efficiency of an organic inhibitor depends on the nature and the state of the metallic surface, chemical composition and structure of the inhibitor. Organic compounds containing nitrogen, sulphur, and oxygen in the conjugated system have been reported as effective inhibitors of aluminium corrosion in different aqueous solutions. The success of an organic compound as a corrosion inhibitor is mainly dependent on its adsorption ability, with the polar groups acting effectively as the centre for the adsorption process [4-7]. The present study is aimed to investigate the efficiency of DPHMPP as a corrosion inhibitor for aluminium in 1.0 N NaOH by weight loss, gasometric, and electrochemical methods.

MATERIALS AND METHODS

Preparation of DPHMPP:
The preparation of DPHMPP was carried out by Claisen-Schmidt condensation. Commercially available vanillin and dihydroxyacetophenone were mixed in a porcelain mortar. Then solid NaOH was added and the mixture was ground with a pestle for about 5-10 minutes. After a few seconds of grinding, the reaction mixture turned yellow and

became pasty [8, 9]. Grinding was continued until the mixture solidified and the solid broke up into small particles. Distilled water was added at the end of the grinding period and the product mixed well with the water. The suspension was vacuum filtered and washed with water using a Buchner funnel and it was allowed to air-dry. The crude product was recrystallized from 95% ethanol. The product was confirmed by Rast method of determining molecular weight and IR spectroscopy.



1-(2,4-Dihydroxy-phenyl)-3-(4-hydroxy-3-methoxy-phenyl)-propenone[DPHMPP]

Weight loss experiments:

The weight loss experiments were carried out with samples of aluminium in the form of sheets with the dimensions, 2 cm×1 cm×0.14 cm, that were cut from commercial pure aluminium. Before each measurement the specimens were polished with different grades of emery papers. The samples were then degreased with acetone and thoroughly washed with deionised water and air dried. The cleaned and weighed aluminium coupons were immersed in 100 ml of 1.0 N NaOH solution, with and without the addition of different concentration of DPHMPP with the aid of glass hooks [10, 11] at 30° and 50°C, respectively. After 1 h immersion, the aluminium specimens were carefully washed with double-distilled water, dried, and then weighed. The weight loss was taken as the difference between the weight at a given time and the initial weight of the test coupon. The average weight loss for three determinations is reported in this study. The surface coverage and inhibition efficiencies were evaluated using the following formulas:

$$\text{Surface coverage, } \theta = \frac{w_o - w_i}{w_o}$$

$$\text{Percentage inhibition efficiency, \%IE} = \frac{w_o - w_i}{w_o} \times 100$$

where, w_o and w_i are the weight losses in uninhibited and inhibited corroding solutions, respectively.

Gasometric method:

Hydrogen evolution measurements were carried out at 30°C, using [12]. The test samples were kept immersed in 100mL of NaOH solution with and without inhibitor in a vessel which allows the measurement of the volume of H_2 evolved. The progress of the corrosion reaction was monitored by the measurement of the volume of hydrogen gas evolved at fixed time intervals. The inhibition efficiency and degree of surface coverage were calculated using the following formulas:

$$\text{Surface coverage, } \theta = 1 - \frac{V'_{Ht}}{V^{\circ}_{Ht}}$$

$$\text{Inhibition efficiency, \%I} = \{1 - \frac{V'_{Ht}}{V^{\circ}_{Ht}}\} \times 100$$

where V'_{Ht} is the volume of hydrogen evolved at time t for inhibited solution and V°_{Ht} is the volume of hydrogen evolved at time t for uninhibited solution.

Electrochemical measurements:

The electrochemical experiments were carried out using Prinstone Electrochemical Analyzer, Model KO264 Micro-cell kit. The aluminium specimens was machine cut into coupons of dimensions 8 cm×1 cm×0.14 cm and embedded in epoxy resin (araldite) leaving a surface area of 1 cm^2 used for electrochemical measurements. A conventional three electrode cell consisting of aluminium as working electrode, saturated calomel electrode and platinum electrode as reference and counter electrodes, respectively, was used. In each measurement a fresh working electrode was used. Several runs were performed for each measurement to obtain reproducible data. The formula used for calculating %IE by electrochemical polarization method was

$$\text{\%IE} = \frac{I_o - I_{inh}}{I_o} \times 100$$

where, I_0 =corrosion current density in absence of inhibitor and I_{inh}=corrosion current density in presence of inhibitor

The inhibition efficiency was calculated from charge transfer resistance values, by the following formula:

$$\%IE = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100$$

where, R_{ct}= charge transfer resistance in the absence of inhibitor and $R_{ct(inh)}$=charge transfer resistance in the presence of inhibitor

RESULTS AND DISCUSSION

Weight loss method:

The difference of the weight loss of aluminium in 1.0 N NaOH solution with and without the addition of various concentration of DPHMPP was determined by weight loss method at 30° and 50°C. At each concentration of the inhibitor the percentage inhibition efficiency was calculated. The calculated values are shown (Table 1). This could be seen from the weight loss decreases with increasing concentration of inhibitor it shows that amount of adsorption and the coverage of the inhibitor on the electrode surface increase with increasing concentration. Thus the electrode surface is efficiently separated from the medium by forming a protective film that blocks the metal surface. The percentage of inhibition efficiency decreases with increase in temperature and it is probably due to the physical adsorption [13-15] of inhibitor on the corroding metal surface.

Table 1: Inhibition of corrosion of aluminium in 0.1N NaOH in the absence and in the presence of inhibitor (DPHMPP) at 30° C and 50° C

Concentration, M	Surface coverage, θ		% IE	
	30°C	50°C	30°C	50°C
1×10^{-4}	0.155	-	15.5	-
1.25×10^{-4}	0.222	-	22.2	-
2.5×10^{-4}	0.456	-	45.6	-
5×10^{-4}	0.511	-	51.1	-
1×10^{-3}	0.556	0.451	55.6	45.1
1.25×10^{-3}	0.644	0.473	64.4	47.3
2.5×10^{-3}	0.689	0.500	68.9	50.0
5×10^{-3}	0.722	0.522	72.2	52.2
7.5×10^{-3}	0.822	0.527	82.2	52.7

ADSORPTION ISOTHERMS

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reaction [16]. The most frequently used isotherms are Langmuir, Temkin, Flory-Huggins and El-Awady adsorption isotherms. All these isotherms are of the general form:

$$f(\theta, x)\exp(-2a\theta) = KC$$

where $f(\theta, x)$ is the configurational factor, θ is the surface coverage degree, C is the inhibitor concentration in the electrolyte, *x* is the size factor ratio, *a* is the molecular interation parameter, and K_{ads} is the equilibrium constant of the adsorption process.

Attempts were made to fit θ values to the isotherms of Langmuir, Temkin, Flory-Huggins and El-Awady et.al.

Langmuir adsorption isotherm

The data obtained from weight loss method was fitted to adsorption isotherm studies, from which regression coefficient, R^2 and K_{ads} were calculated and the calculated values are shown (Table.2). The R^2 values are very close to unity, indicating strong adherence to Langmuir adsorption isotherm. A plot of C/θ vs C at various temperatures is shown [Fig.1]. The resulting parallel lines at different temperature confirm that inhibition was due to the monolayer

adsorption of DPHMPP on the metal surface. The deviation of slope value from the unity may be reveals on the basis of the interaction among the adsorbed species on the metal surface [17, 18, 19]

El-Awady adsorption isotherm

The calculated K_{ads} and $1/y$ values are given (Table 2). The $1/y$ value shows that given inhibitor occupies more than one active site on the metal surface. The value of K_{ads} decreases with increase in temperature indicating that adsorption of DPHMPP inhibitor on the aluminium surface was unfavorable at higher temperature and it conforms to physisorption. A plot of $log\left(\frac{\theta}{1-\theta}\right)$ $vs\ logC$ at various temperature are shown [Fig.2]

Temkin adsorption isotherm

The values of surface coverage (θ) were plotted against logC for various concentrations of DPHMPP [Fig.3]. The straight line indicates that the adsorption of inhibitor on the aluminium surface follows Temkins adsorption isotherm in alkaline medium. The negative value of 'a' shows repultion present in the adsorption layer [20].

Flory-Huggins adsorption isotherm

Flory-Huggins adsorption parameters such as regression coefficient, R^2, size parameter, x, were calculated and the results are shown (Table.2). The plot of $\log\frac{\theta}{c}$ against $log(1-\theta)$ is linear (Fig.4) showing that Flory-Huggins isotherm was obeyed.

Table 2: Langmuir, El-Awady, Temkins and Flory Huggins adsorption parameters for adsorption of DPHMPP inhibitor on aluminium in alkaline medium

Adsorption isotherm	Temperature (°C)	K_{ads}, M^{-1}	$-\Delta G^0_{ads}$ kJ mol^{-1}	R^2	slope	1/y	-a	x
Langmuir	303 323	2095.29 -	29.387 -	0.9926 1.0000	1.63 1.85			
El-Awady	303 323	1439.79 332.56	28.442 24.750	0.9996 0.9975		1.6 6.8		
Temkins	303 323	53995.72 -	37.573 -	0.9922 0.9965			8.8 14.2	
Flory Huggins	303 323	3.5115 5.9318	20.225 12.920	0.9960 0.9984				5.1 13.0

Fig.1. Langmuir adsorption isotherm for corrosion of aluminium in 1.0 N NaOH containing different concentration of DPHMPP

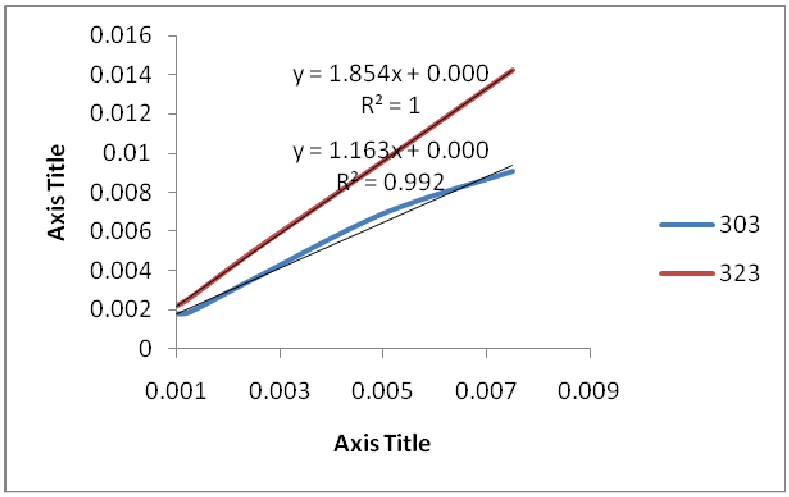


Fig.2. El-Awady adsorption isotherm for corrosion of aluminium in 1.0N NaOH containing different concentration of DPHMPP

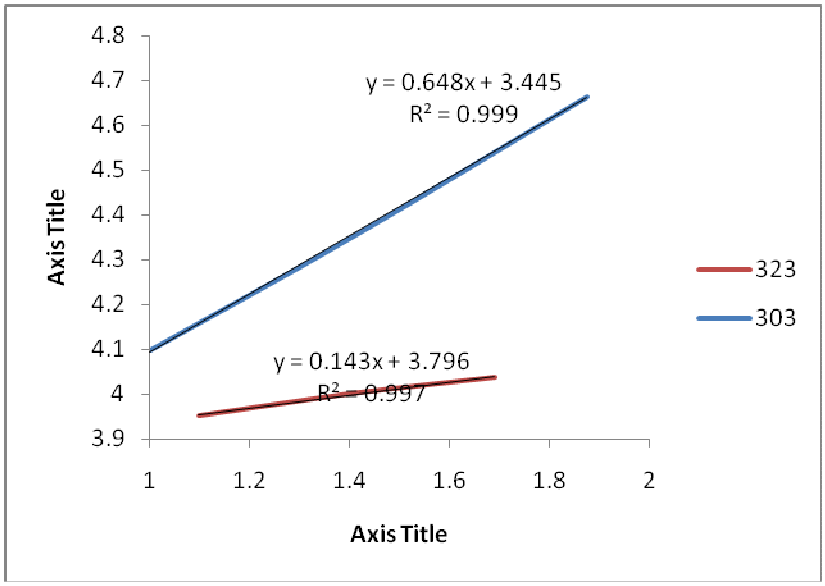


Fig.3.Temkins adsorption isotherm for corrosion of aluminium in 1.0N NaOH containing different concentration of DPHMPP

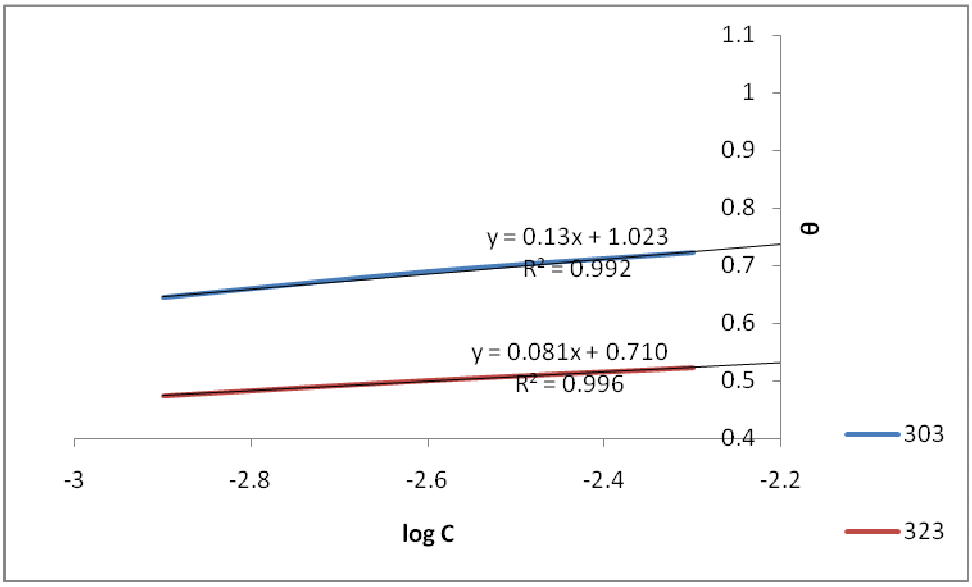
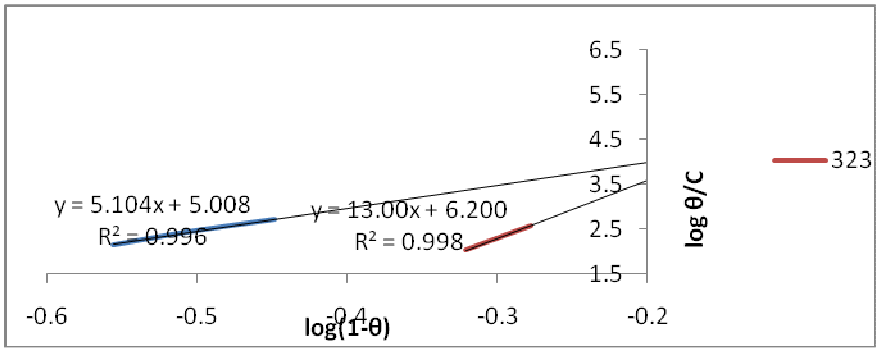


Fig.4. Flory-Huggins adsorption isotherm for DPHMPP in 1.0N NaOH solutions



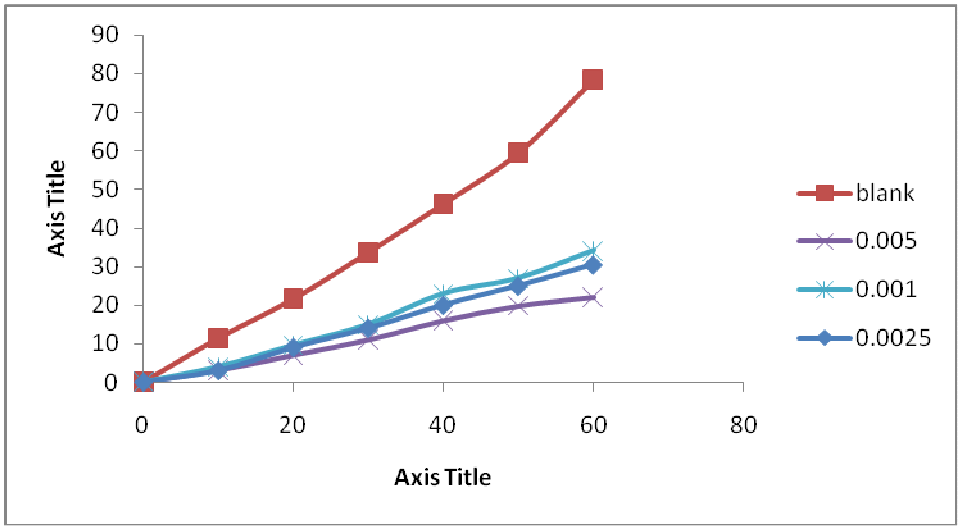
Gasometric method

The volume of hydrogen gas evolved during the corrosion of aluminium in 1.0 N NaOH solution measured as a function of the reaction time and the data are represented graphically (Fig.). It is obvious that the volume of hydrogen gas evolved decreases with increase in the concentration of DPHMPP indicating that the protection ability of inhibitor was concentration dependent. [21, 22]. The calculated values are given (Table.3). There is good agreement between the %IE values determined by weight loss and gasometric method.

Table:3

Concentration(M)	%IE
1×10^{-3}	56.6
2.5×10^{-3}	61.3
5×10^{-3}	71.9

Fig.5.Volume of Hydrogen gas evolved with time



Synergistic effect:

The synergistic parameter S_θ was calculated by the following formula

$$S_\theta = (1-\theta_{1+2})/(1-\theta'_{1+2})$$

where θ_1 is the surface coverage by anion, θ_2 is the surface coverage by cation and θ'_{1+2} is the surface coverage by both anion and cation. Synergistic effect of tetrabutylammoniumbromide (TBAB) increased the inhibition efficiency of the DPHMPP, in 1.0 N NaOH. The synergistic effect is due to the electrostatic interaction with inhibitor and TBAB higher the surface coverage and greater the corrosion inhibition. The synergistic effect results are given (Table 4). It is clear the inhibition efficiency synergistically increases on addition of 0.00075M TBAB to different concentrations of DPHMPP.

Table 4: Inhibition of corrosion of aluminium in 0.1 N NaOH in the presence of DPHMPP +0.00075M TBAB mixture

Concentration, M	%IE	S_θ
TBAB(0.00075)	9.0	
1×10^{-4}+TBAB	64.7	2.1
1.25×10^{-4}+TBAB	69.1	2.2
2.5×10^{-4}+TBAB	75.0	1.8
5×10^{-4}+TBAB	69.0	1.3
1×10^{-3}+TBAB	72.0	1.3

Electrochemical methods

Potentiodynamic polarization method

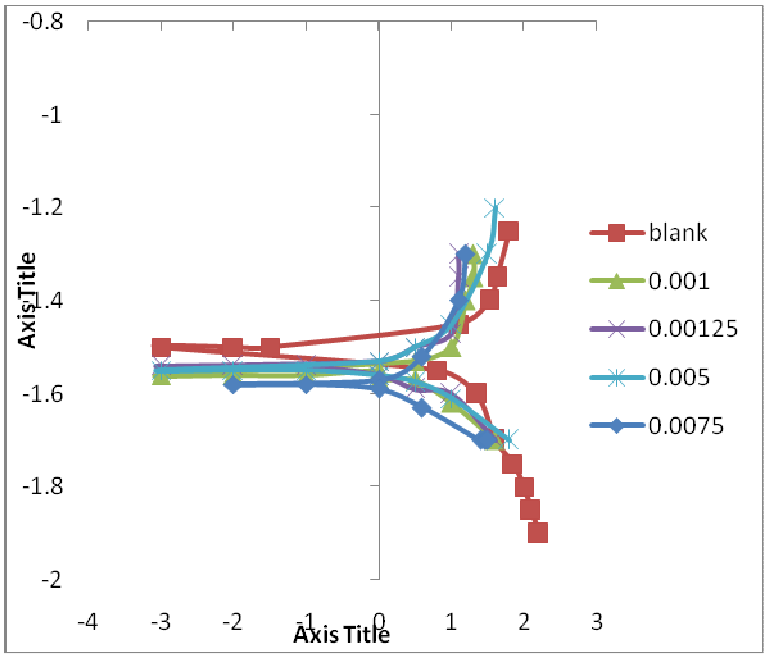
Corrosion potentials, $E_{corr,}$ corrosion current densities, $I_{corr,}$ and percentage inhibition efficiency are shown (Table 5). The data reveals that the addition of the inhibitor shifts the corrosion potential slightly in the positive direction and reduces both anodic and cathodic current densities, which is indicating that DPHMPP suppresses the electrode reactions especially the inhibitor inhibits the anodic dissolution. These results indicate that inhibitor acts as mixed type. It is clear from Table that the values of b_c and b_a has small changes with increasing DPHMPP concentration

which indicate that these inhibitor act by simple blocking the available surface area for both anodic and cathodic processes.

Table 5: potentiodynamic polarization parameters for different concentration of DPHMPP **in 1.0N NaOH**

Concentration, M	$-E_{corr}$, V	I_{corr}, mA cm^{-2}	b_c, mV dec^{-1}	b_a, mV dec^{-1}	%IE
Blank	1.592	16135.63	270.5	496.5	
1×10^{-3}	1.563	7117.95	190.0	485.4	55.9
1.25×10^{-3}	1.539	5670.05	251.6	497.0	64.9
5×10^{-3}	1.544	4797.40	223.0	528.5	70.3
7.5×10^{-3}	1.570	3815.99	186.1	491.0	76.4

Fig.6. Tafel plot



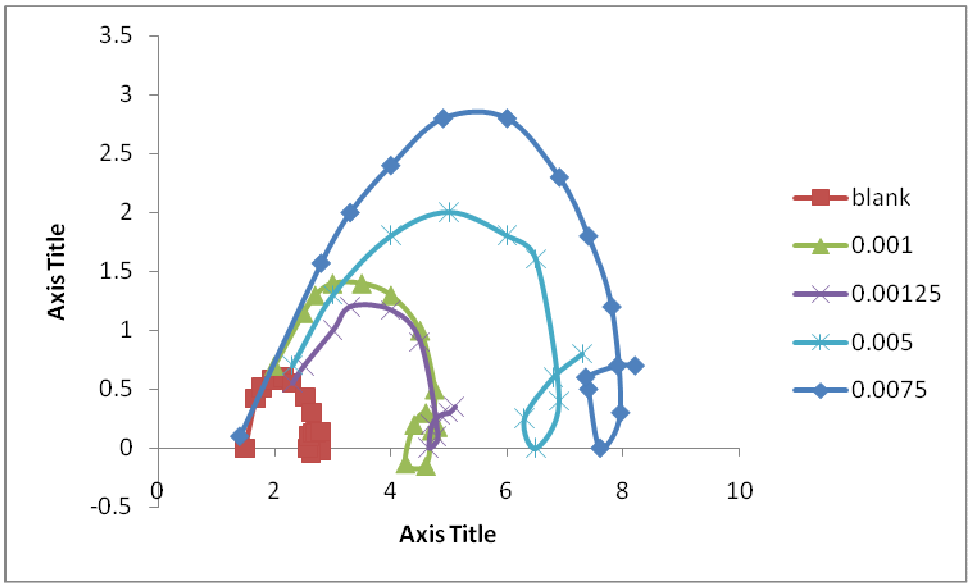
Impedance method

Impedance measurements have been carried out for aluminium in the alkaline solution in the absence and presence of the DPHMPP at OCP The inhibition efficiency with respect to R_{ct} values are given (Table 6). Nyquist plots of aluminium in 1.0 N NaOH, in the absence and presence of different concentrations of DPHMPP, are shown (Fig.7). The each impedance diagram consist of a large capacitive loop at high frequency, it is assigned to the relaxation process in the aluminium oxide film presents on the aluminium surface and its dielectic properties [23, 24]. A small inductive loop at medium frequency followed by initiation of second capacitive loop at low frequency values could be assigned to the metal dissolution. The value of R_{ct} increases and C_{ct} decreases with the increase in concentration of DPHMPP indicate that the corrosion of aluminium in 1.0 N NaOH is controlled by a charge transfer process and the corrosion inhibitor occurs through the adsorption of DPHMPP on aluminium surface [25,26].

Table 6: EIS measurements for different concentration of DPHMPP in alkaline medium

Concentration, M	R(ohm)	C_{dl} (μF)	%IE
Blank	0.9075	55.5	
1×10^{-3}	2.469	43.93	63.2
1.25×10^{-3}	2.534	62.7	64.4
5×10^{-3}	4.175	38.06	78.3
7.5×10^{-3}	4.555	23.55	80.1

Fig.7. Nyquist plot



SEM Technique

Scanning electron micrographs (SEM) of the aluminium surface in 1.0 N NaOH solution with and without HMPHPP are shown (Fig.8a, 8c & 8b). It is clear from the figure the inhibited metal surface is smoother than the uninhibited surface, it proves that a protective layer formed over the metal surface and preventing the attack of NaOH.

Fig.8a SEM photograph of aluminium before immersed in NaOH solution

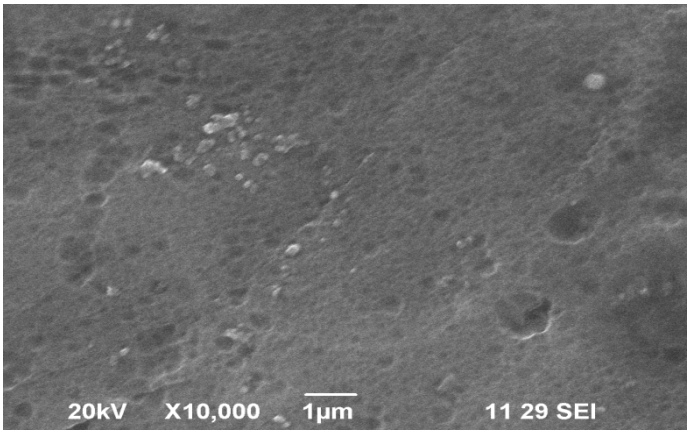


Fig.8b SEM photograph of aluminium after immersed in 1.0 N NaOH solution

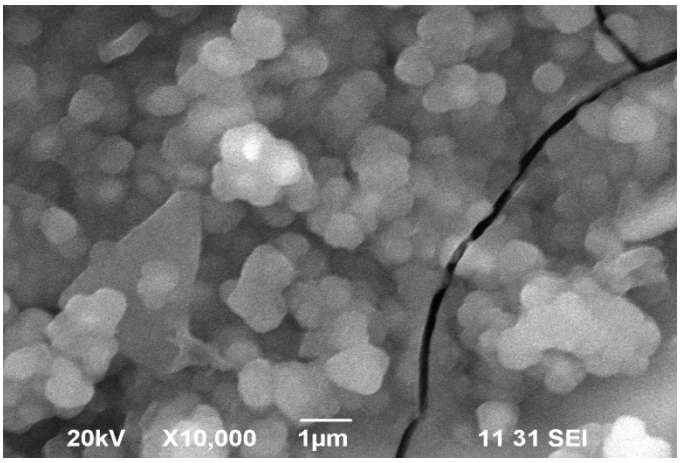
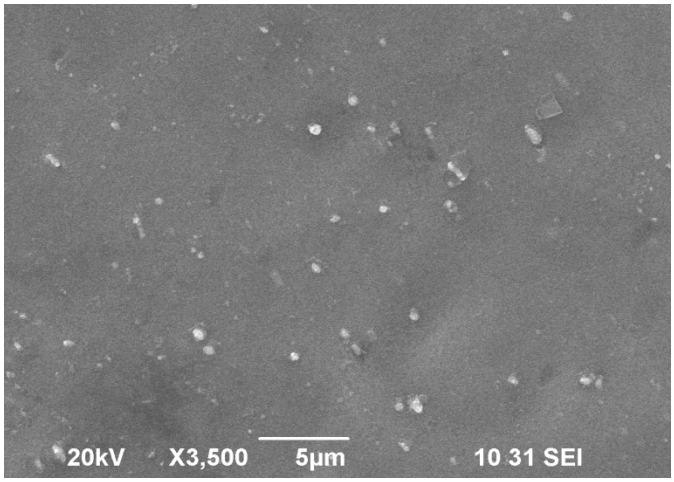


Fig.8c SEM photograph of aluminium after immersed in 1.0 N NaOH in presence of DPHMPP



CONCLUSION

1. [1-(2,4-dihydroxy–phenyl)-3-(4-hydroxy-3-methoxy-phenyl)-propenone] (DPHMPP) showed a maximum of 82.2% inhibiton of aluminium corrosion in alkaline medium.
2. Inhibition efficiency increases with increasing concentration and higher the temperature the lower the inhibition efficiency.
3. It was found that the hydrogen evolution suppressed by the addition of inhibition by gasometric method
4. Additions of TBAB increase the inhibition efficiency DPHMPP The process of adsorption of the inhibitor obeys the entire four adsorption isotherm discussed.
5. The inhibitor was found to be of mixed type.
6. The mechanism of adsorption appears to be physisorption.

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