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Research Article

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The inhibition effect of [3-(4-hydroxy-3-methoxy-phenyl)-1-phenyl-propenone] on the corrosion of the aluminium in alkaline medium

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ABSTRACT

Corrosion behavior of aluminium in 1.0N NaOH containing 3-(4-hydroxy-3-methoxy-phenyl)-1-Phenyl-propenone [HMPPP] was studied using chemical and electrochemical techniques. The protective effects of inhibitor have been investigated. The inhibition efficiency of the inhibitor increased with the increasing concentration of the inhibitor. The maximum inhibition efficiency was 63%. The results from weight loss and electrochemical methods are in good agreement. But the inhibition efficiency decreased with the increase of temperature. The inhibitor was mixed type and it was found to obey Langmuir and El-Awady adsorption isotherms.

Keywords: Aluminium corrosion, Inhibitor, Weight loss method, Electrochemical method, Adsorption isotherm

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INTRODUCTION

Aluminium is the second most used metal after iron. Because of its low atomic mass and the high negative value of the standard electrode potential, aluminium can be used as an anode material for power sources with high energy densities [1]. The corrosion behavior of aluminium in alkaline solution have been extensively studied in the development of the aluminium anode for the aluminium/air battery [2,3]. Aluminium corrosion in alkaline medium is characterized by rapid effervescence in which the hydrogen gas evolution provides self-agitation at the interface and disperses the corrosion products.

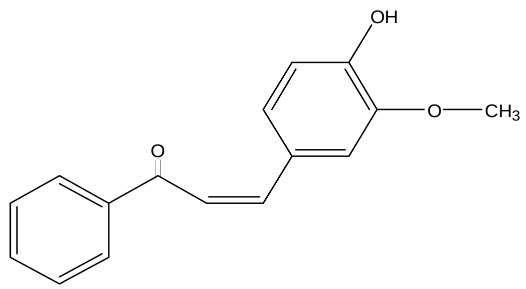
The important strategy to avoid corrosion is to isolate the metal from corrosion agents and it is performed by the application of corrosion inhibitors. The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to be absorbed on the metal surface. Organic compounds containing heteroatoms such as nitrogen, sulphur or oxygen in the conjugated system are found to be powerful inhibitors of metal in aqueous medium. Most of the effective organic inhibitor used in industry has heteroatoms with multiple bond through which they can adsorb on the metal surface [4-7]. The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to be adsorbed on the metal surface.

The aim of present study is to investigate the corrosion inhibitive property of HMPPP by weight loss method and elctrochemical techniques and to find out the synergistic effect of adding tetrabutylammonium bromide to the inhibitor, HMPPP.

EXPERIMENTAL SECTION

Preparation of HMPPP
Commercially available vanillin (0.05 mole) and acetophenone (0.05 mole) were mixed in a porcelain mortar. Then solid NaOH (0.01 mole) 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. Then distilled water (10 mL) 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 and IR spectroscopy.



3-(4-Hydroxy-3-methoxy-phenyl)-1-phenyl-propenone(HMPPP)

Preparation of aluminium coupons

Commercially pure aluminium strips, with the dimensions, 2 cm×1 cm×0.14 cm, were used for the investigation. Before each measurement the specimens were polished with different grades of emery papers for weight loss method. 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 for electrochemical measurements. The samples were then degreased with acetone and thoroughly washed with deionised water and air dried.

Weight loss measurements

The cleaned and weighed aluminium coupons were suspended in beakers containing 100 ml of aerated, unstirred 1.0N NaOH solution, without and with the inhibitor, for a stipulated period of time with the aid of glass hooks and rods [10,11] at 30° and 50 °C, respectively. The aluminium samples were then removed from the solution, cleaned by brushing under running tap water to remove the corrosion products, dried and reweighed to determine the weight loss. The surface coverage and inhibition efficiencies were evaluated using the formulas:

Surface coverage, $\theta = \frac{w_0 - w_i}{w_0}$

Percentage inhibition efficiency, %IE= $\frac{w_0 - w_i}{w_0} \times 100$

where, w_0 and w_i are the weight losses in uninhibited and inhibited corroding solutions, respectively.

Electrochemical measurements

Electrochemical experiments were carried out with Princeton Applied Research Electrochemical Analyzer, Model KO264 Micro-cell kit. 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. Before measurement the working electrode was immersed in test solution for about 45 min. until a steady open circuit potential (OCP) was reached. The polarization measurements were carried out by polarizing the electrode from -1.9 V to -1.1 V with respect to the OCP at a scan rate of 10 mV s^{-1} .The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential(E_{corr}) to obtain the current densities(I_{corr}). 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:

$$\%IE = \frac{I_0 - I_{inh}}{I_0} \times 100$$

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

EIS measurements were carried in 100KHz-10Hz frequency range at OCP at 30±1°C. The inhibition efficiency was calculated from charge transfer resistance values, using the 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

RESULT AND DISCUSSION

Rast method

The molecular weight was determined by Rast method (mol. wt.255) for HMPPP and it is almost equal to the formula weight of 254. The IR spectrum of compound show (OH) peak at 3793.6 cm^{-1}, $C = C$ peak at 1667.21 cm^{-1} and the peak for $C = O$ conjugated with phenyl ring was at 1598.2cm^{-1}. It conforms the formation of product HMPPP.

Weight loss method

The percentage inhibition efficiency of HMPPP has been evaluated by weight loss method at 30° and 50°C (Table 1). It was observed to increase with increase in concentration of the inhibitor and this behavior indicates that the adsorbed inhibitor molecules formed a barrier film on the aluminium surface [12], and it decreases with increase in temperature. According to Ferrreira et. al. [13] decrease in inhibition efficiency with increase in temperature indicates physisorption of inhibitor on the corroding metal surface. It is also attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of the metal [14,15].

Table 1: Corrosion parameter for aluminium in 1.0N NaOH in the absence and in the presence of inhibitor(HMPPP) at difference temperatures

Temperature, (°C)	[HMPPP], M	Surface coverage, θ	% IE
30	5×10^{-4}	0.079	7.9
	7.5×10^{-4}	0.092	9.2
	1×10^{-3}	0.355	35.5
	2.5×10^{-3}	0.434	43.4
	5×10^{-3}	0.513	51.3
	7.5×10^{-3}	0.579	57.9
	1×10^{-2}	0.605	60.5
	1.25×10^{-2}	0.635	63.5
50	2.5×10^{-3}	0.274	27.4
	5×10^{-3}	0.421	42.1
	7.5×10^{-3}	0.537	53.7
	1×10^{-2}	0.567	56.7
	1.25×10^{-2}	0.604	60.4

ADSORPTION ISOTHERMS

Langmuir adsorption isotherm

The weight loss data were fitted to Langmuir isotherm equation which can be expressed as:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

where, C is the concentration of the inhibitor, K_{ads} is the adsorption equilibrium constant and θ is degree of surface coverage by the inhibitor. A plot of C/θ vs C is linear (Fig.1). The values of regression coefficient, R^2 and K_{ads} are shown (Table 2). The values of R^2 indicate strong adherence of the corrosion inhibition process to Langmuir adsorption isotherm.

El-Awady adsorption isotherm

It is expressed as:

$$\log\left(\frac{\theta}{1-\theta}\right) = logK + y\, logC$$

Here $K_{ads,}$ the equilibrium constant of adsorption process, is calculated by the relationship, $K_{ads} = K^{1/y}$. A plot of $log\left(\frac{\theta}{1-\theta}\right)\ vs\ logC$ is linear (Fig. 2). The calculated K_{ads} and $1/y$ values are given (Table 2). The value of $1/y$ shows that one inhibitor molecule occupies one active site on the metal surface. The value of K_{ads} decreases with increase in temperature indicating that adsorption of HMPPP inhibitor on the aluminium surface was unfavorable at higher temperature and this observation also conforms to physisorption.

Table 2: Langmuir and El-Awady adsorption parameters for adsorption of HMPPP inhibitor on aluminium in 1.0N NaOH

Temperature (°C)	Langmuir isotherm				El-Awady isotherm			
	K_{ads}, M^{-1}	$-\Delta G^0_{ads}$ kJ mol^{-1}	slope	R^2	K_{ads}, M^{-1}	$-\Delta G^0_{ads}$ $kJmol^{-1}$	1/y	R^2
30	231.27	23.84	1.19	0.90	191.99	23.37	1.13	0.85
50	166.97	23.01	1.16	0.98	138.60	22.55	1.13	0.98

Fig.1. Langmuir adsorption isotherm for corrosion of aluminium in 1 N NaOH containing different concentrations of HMPPP

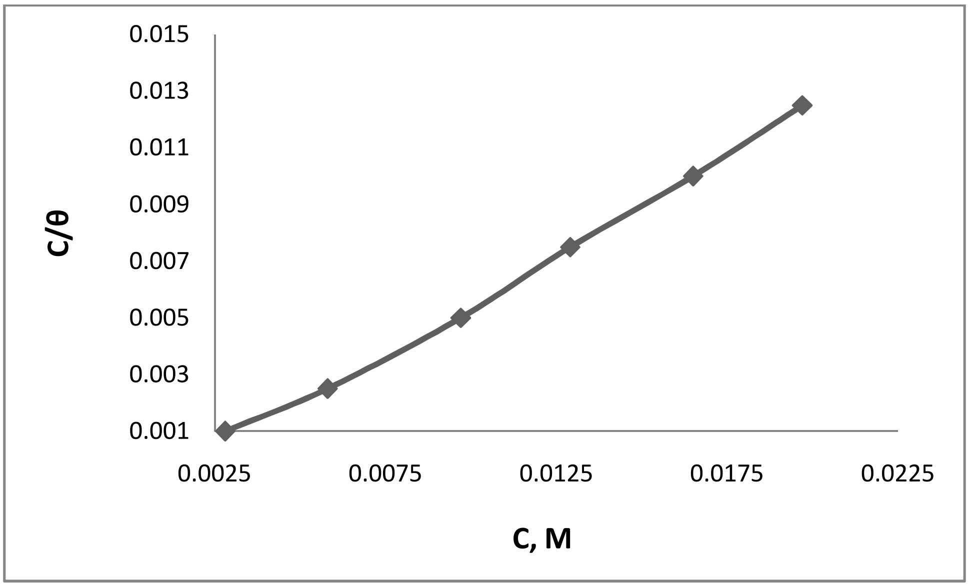
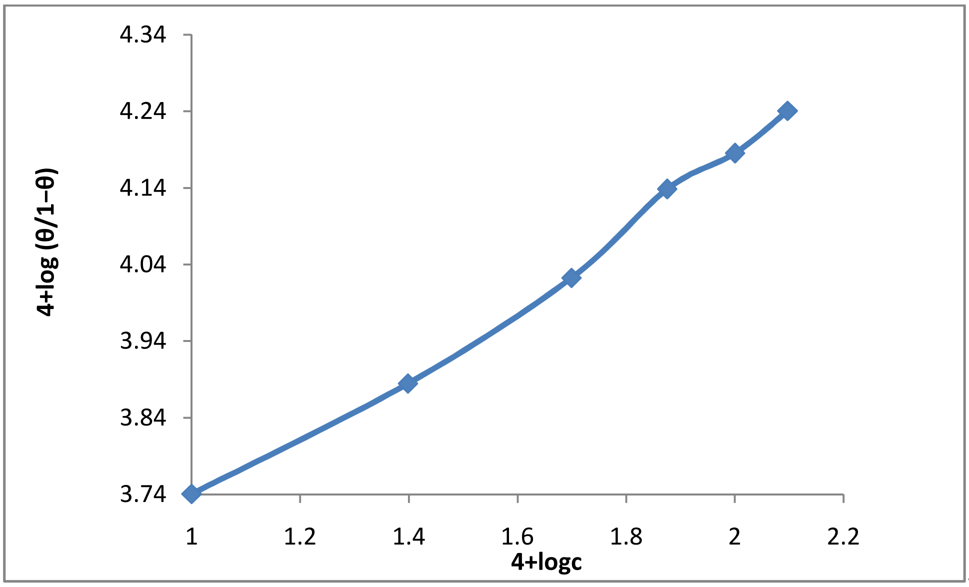


Fig.2. El-Awady adsorption isotherm for corrosion of aluminium in 1.0N NaOH containing different concentrations of HMPPP



Synergistic effect

The inhibitor HMPPP was observed to inhibit considerably the corrosion of aluminium in alkaline medium. A further increase in percentage of inhibition of corrosion was observed on the addition of 0.00075M tetrabutylammoniumbromide(TBAB) to each concentration of inhibitor. The synergetic effect results are given

(Table 3). It is clear that the inhibition efficiency synergistically increases on addition of 0.00075M TBAB to different concentrations of HMPPP.

Table 3: Synergistic parameter for the inhibition of corrosion of aluminium in 1.0N NaOH in the presence of inhibitor + 0.00075M TBAB mixture

[HMPPP], M	%IE	S_0
TBAB(0.00075)	9.0	
5×10^{-4}+TBAB	77.1	3.6
7.5×10^{-4}+ TBAB	72.9	3.0
1×10^{-3}+ TBAB	76.0	2.3
2.5×10^{-3}+ TBAB	71.9	1.7
5×10^{-3}+ TBAB	77.1	1.7

Electrochemical methods
Potentiodynamic polarization method

Corrosion potentials, $E_{corr,}$ corrosion current densities, $I_{corr,}$ and percentage inhibition efficiency are shown (Table 4). Representative current-potential curves (Tafel plot) for aluminium in 1.0N NaOH with and without HMPPP are given (Fig. 3). With an increase in the concentration of HMPPP in alkaline medium, the curves are gradually shifted towards lower current density. The corrosion potential also slightly shifted towards negative direction on increasing the concentration of the inhibitor. It is realized from these observation that the inhibitor molecule retard the corrosion process without changing the mechanism of corrosion process in the medium of investigation and it also conforms the inhibitive property of the inhibitor is concentration dependent. The inhibitor [HMPP] affect both anodic as well as cathodic sites, so inhibitor acts as mixed type inhibitor for corrosion of aluminium in 1.0N NaOH. The percentage of inhibition efficiency calculated from I_{corr} values agreed with the values obtained from weight loss method.

Table 4: potentiodynamic polarization parameters for aluminium in 1.0N NaOH with different concentrations of HMPPP

[HMPPP],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	
7.5×10^{-4}	1.506	14385.44	187.6	413.3	10.8
1.0×10^{-3}	1.561	9131.88	110.5	489.7	43.4
2.5×10^{-3}	1.547	8669.64	124.5	471.2	46.3
1.25×10^{-2}	1.583	6548.33	222.1	394.3	59.4

Impedeance method

The values of charge transfer resistance and double layer capacitance and percentage inhibition efficiency are given (Table 3). Nyquist plots of aluminium in 1.0N NaOH, in the absence and presence of different concentrations of HMPPP, are shown (Fig.4). It is clear that the value of R_{ct} increases on increasing the concentration of the inhibitor, indicating that the corrosion rate decreases in presence of the inhibitor. It is also clear that the value of C_{dl} decreases on addition of inhibitor, indicating that the increase in the thickness of the electrical double layer, suggesting that the inhibitor molecule formed protective double layer at the metal surface. It is observed that the diameter of the semicircle increases with increasing HMPPP concentration. The increase in the diameter of the capacitive semicircles with increasing concentration of inhibitor suggests that the inhibition action of the inhibitor is due to its adsorption on the metal surface without altering the corrosion mechanism.

Table 3: EIS measurements for Al in 1.0N NaOH in the absence and presence of different concentrations of HMPPP

[HMPPP], M	$R_{ct,}$ ohm	$C_{dl,}$ μF	%IE
Blank	0.9075	55.5	
7.5×10^{-4}	1.07	0.4713	15.2
1.0×10^{-3}	1.391	0.1902	34.6
2.5×10^{-3}	1.791	0.1908	49.3
1.25×10^{-2}	2.809	-	67.7

Fig.3. Tafel plot

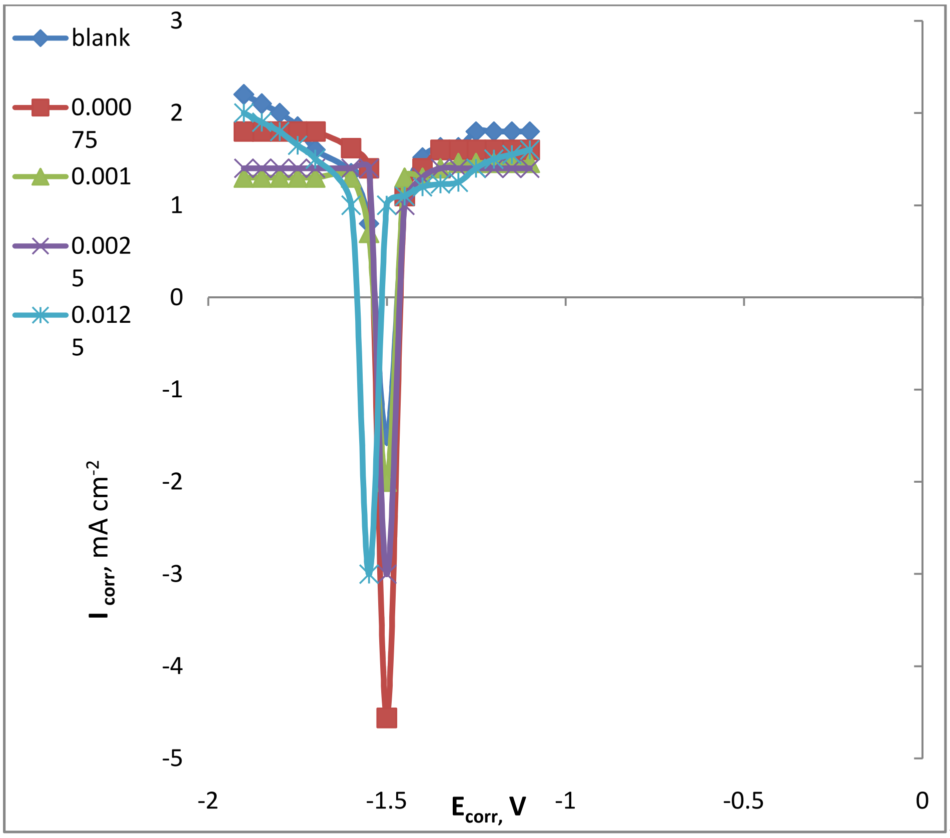
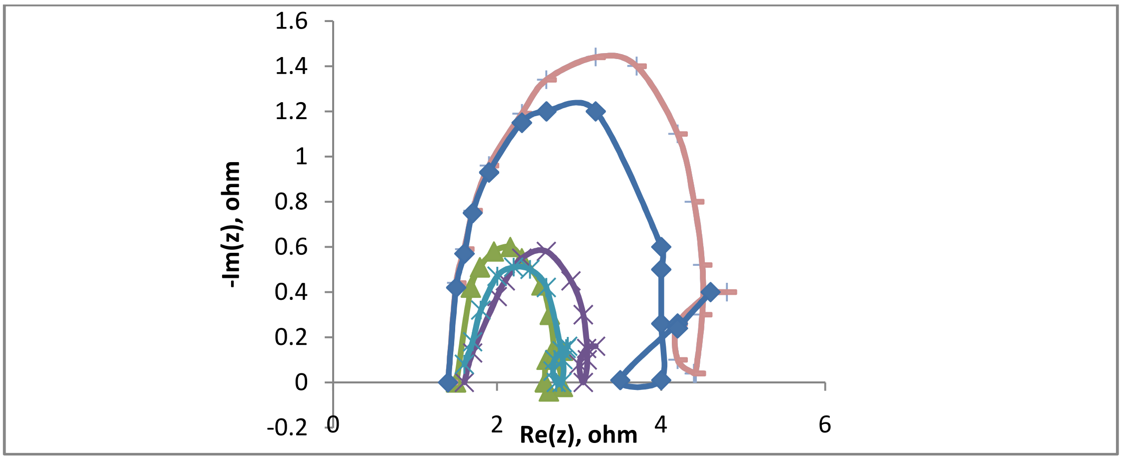


Fig.4. Nyquist plot



CONCLUSION

1. 3-(4-hydroxy-3-methoxy-phenyl)-1-Phenyl-propenone(HMPPP) showed a maximum of 63% inhibiton of aluminium corrosion in alkaline medium.
2. The inhibitor was found to be of mixed type.
3. Additions of TBAB to HMPPP, resulted in synergistic effect.
4. The process of adsorption of the inhibitor obeys the Langmuir and El-Awady et al. adsorption isotherms.
5. The mechanism of adsorption appears to be physisorption.

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