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

[1]N Santhini, [2]T Jeyaraj

[1]*PG & Research Dept. Chemistry, Bishop Heber College (Autonomous), Tiruchirappalli*
[2]*PG & Research Dept. of chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli*
_____

ABSTRACT

The inhibition effect of [3-(4-hydroxy-3-methoxy-phenyl)-1-(2-hydroxy-phenyl-propenone (HMPHPP) on aluminium metal in 1.0 N NaOH was studied by weight loss, polarization measurements and SEM technique. The inhibition efficiency was found to increase with increasing concentrations of the inhibitor. The maximum inhibition efficiency was 72.5%. The effect of temperature on the corrosion inhibition was studied and the inhibition efficiency was found to decrease with the increase of temperature. The inhibitor was mixed type and it was found to obey Langmuir, El-Awady, Temkins and Flory Huggins adsorption isotherms.

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

INTRODUCTION

Aluminium is widely used in various industrial operations because of its light weight, relatively high mechanical strength and good corrosion resistance. The pickling of aluminium in NaOH/KOH for the purpose of degreasing prior to anodizing or to give a matte finish is a common practice. Alkalis destroy the protective skin of Al_2O_3 over the metal surface and dissolve the metal at a high rate. Therefore pickling inhibitors compatible with alkalis, are needed Thus study of corrosion inhibition of aluminium in alkaline medium has gained great importance in recent years [1-3].

The use of organic inhibitors containing sulphur, nitrogen and oxygen atoms are retarding the corrosion. The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface [4-7]. The lone pair of electrons in hetero atoms determines the adsorption of these molecules on the metal surface. In the present work the effect of various concentrations of HMPHPP as corrosion inhibitor for aluminium in 1.0 N NaOH was studied by chemical, electrochemical and SEM techniques.

MATERIALS AND METHODS

Preparation of HMPHPP:
The compound HMPHPP was synthesized by solvent free synthesis as given below. The aromatic aldehyde such as vaniline and monohydroxyacetophenone were mixed with solid NaOH 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. The crude product was recrystallized by 95% ethanol. The product was confirmed by Rast method of molecular weight determination IR and UV spectra.

_____
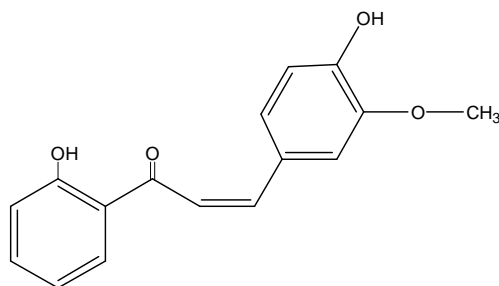
3-(4-Hydroxy-3-methoxy-phenyl)-1-(2-hydroxy-phenyl)-propenone (HMPHPP)

Chemical measurements:

The chemical measurements were carried out by two methods; weight loss method and gasometric method. It was performed with samples of aluminium in the form of sheets with the dimensions, 2 cm×1 cm×0.14 cm, that were cut from commercially 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.

Weight loss method:

The cleaned and weighed aluminium coupons were immersed in 100 ml of 1.0 N NaOH with and without the addition of different concentrations of HMPHPP with the aid of glass hooks [10, 11] at 303K and 323K, respectively. After 1 h immersion, the aluminium specimens were carefully washed in double-distilled water, dried, and then weighed. The weight loss data were obtained from the average value of three parallel samples in 1.0 N NaOH with and without inhibitor at different concentrations.

Gasometric method:

Hydrogen evolution measurements were carried out at 303K. The inhibition efficiency and degree of surface coverage were calculated from the volume of hydrogen evolved per minute.

Electrochemical measurements:

The potentiodynamic polarization (PDP) and impedance measurements (EIS) were carried out using Prinstone Electrochemical Analyzer, Model KO264 Micro-cell kit. The aluminium specimens were 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 of 1cm^2 area, 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. Tafel curves were obtained by changing the potential from -1.7 mV to -1.1 mV with scan rate of 10m V/sec. 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. EIS measurements were carried out in frequency range from 100 kHz to 10 kHz.

<div align="center">

RESULTS AND DISCUSSION

</div>

Rast method:

The molecular weight was determined by Rast method (mol. wt.271) for HMPHPP and it is almost equal to the formula weight of 270. The UV-visible adsorption band around 259&361nm indicates [(π-π^*) & (n-π^*) transition] presence of α, β-unsaturated compound. The IR spectrum of compound show OH peak at 3396 cm^{-1}, C=C peak at 1675 cm^{-1} conjugation of C=O with phenyl ring at 1538.17 cm^{-1}.

Weight loss method:

The percentage inhibition efficiency (%IE) of the aluminium corrosion by 1.0 N NaOH for various concentrations of HMPHPP at 303K and 323K was determined by following formula:

Surface coverage, $\theta = \frac{w_0 - w_i}{w_0}$ _____ (1)

Percentage inhibition efficiency, %IE= $\theta \times 100$ _____ (2)

_____

where, w_0 and w_i are the weight losses in uninhibited and inhibited corroding solutions respectively. The calculated values are shown (Table 1). It is clear from table 1 inhibition efficiency increases with increase in concentration of the inhibitor and it indicates that the adsorbed inhibitor molecules forming a protective adsorption film [12] that blocks the metal surface, separating it from the corrosive medium. It was observed that inhibition efficiency decreases with increase in temperature and this decrease in inhibition efficiency with increase in temperature can be attributed to the decrease in the protective nature of the inhibitive film formed on the metal surface at higher temperature [13,14] and it also indicates physisorption[15] of inhibitor on the corroding metal surface.

Table 1: Corrosion parameter for aluminium in 0.1N NaOH in the absence and in the presence of inhibitor (HMPHPP) at difference temperatures

Concentration, M	Surface coverage, θ		% IE	
	303K	323K	303K	323K
1×10^{-4}	0.100	-	10.0	-
1.25×10^{-4}	0.125	-	12.5	-
2.5×10^{-4}	0.250	-	25.0	-
5×10^{-4}	0.375	-	37.5	-
7.5×10^{-4}	0.450	0.072	45.0	7.2
1×10^{-3}	0.525	0.081	52.5	8.1
1.25×10^{-3}	0.600	0.090	60.0	9.0
2.5×10^{-3}	0.625	0.117	62.5	11.7
5×10^{-3}	0.725	0.143	72.5	14.3

ADSORPTION ISOTHERMS
The mechanism of interaction of the inhibitor and the metal can be explained using various adsorption isotherm namely Langmuir, Temkin, Flory-Huggins and El-Awady adsorption isotherms. All these isotherms are of the general form:

$$f(\theta, x)\exp(-2a\theta) = KC \underline{\hspace{2cm}} (3)$$

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 interaction parameter, and *K* is the equilibrium constant of the adsorption process. The type of adsorption of inhibitor was elucidated from the degree of surface coverage value (θ) which is calculated from the equation (1) and the values are [16] shown (Table.2).

Langmuir adsorption isotherm
The Langmuir adsorption isotherm is given by:

$C/\theta = 1/K_{ads} + C \underline{\hspace{2cm}} (4)$

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. The values of regression coefficient, R^2 and K_{ads} are shown (Table.2). Comparing the values of R^2, it is seen that Langmuir adsorption isotherm is best applicable at 323K than at 303K. This confirms that the adsorption behavior of the inhibitor is strongly influenced by temperature. A plot of C/θ vs. C at various temperature is shown [Fig.1]. The resulting parallel lines at different temperature confirm that inhibition was due to the adsorption of HMPHPP on the metal surface [17]. The deviation of slope value from the unity indicates there is no interaction among the adsorbed species.

El-Awady adsorption isotherm
It is given by the expression:

$$\log\left(\frac{\theta}{1-\theta}\right) = logK + y\,logC \underline{\hspace{2cm}} (5)$$

HereK_{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 $1/y$ is greater than one showing that given inhibitor occupies more than one active site on the metal surface. The value of

2215

K_{ads} decreases with increase in temperature indicating that adsorption of HMPHPP inhibitor on the aluminium surface was unfavorable at higher temperature and it conforms to physisorption.

Temkin adsorption isotherm
It is given by the expression:

$$\theta = \frac{-2.303 \log K}{2a} - \frac{2.303 \log C}{2a} \underline{\hspace{3cm}}(6)$$

Where K is the adsorption equilibrium constant, 'a' is the lateral interaction parameter. The plot of θ against log C at various temperatures are shown [Fig.3]. The linear plot indicate that Temkin adsorption isotherm was obeyed and negative value of 'a' indicated repulsion exists in the adsorption layer [18].

Flory-Huggins adsorption isotherm
It is given by the expression:

$$\log\frac{\theta}{c} = \log K + x\log(1-\theta) \underline{\hspace{3cm}}(7)$$

where 'x' is the size parameter and it is a measure of the number of adsorbed water molecules substituted by an inhibitor molecule. The plot of $\log\frac{\theta}{c}$ against $\log(1-\theta)$ is linear (Fig.4) showing that Flory-Huggins isotherm was obeyed. The adsorption parameters are shown [Table.2].

Table 2: Adsorption parameters for the adsorption of HMPHPP inhibitor on aluminium in 1.0 N NaOH

Adsorption isotherm	Temperature (°C)	K_{ads}, M^{-1}	$-\Delta G^0_{ads}$ kJ mol^{-1}	R^2	slope	1/y	-a	x
Langmuir	303	1178.13	27.935	0.994				
	323	151.86	22.773	0.9988				
El-Awady et al	303	914.03	27.295	0.9645	1.425	1.21	2.9	2.1
	323	2.565	12.492	0.9948	5.71	2.4	13.2	14.9
Temkins	303	18849.04	34.920	0.9791				
	323	8682.07	32.967	0.9994				
Flory Huggins	303	101.678	27.263	0.9055				
	323	1.4614	11.077	0.9984				

Fig.1. Langmuir adsorption isotherm for corrosion of aluminium in 1.0 N NaOH containing different concentrations of HMPHPP
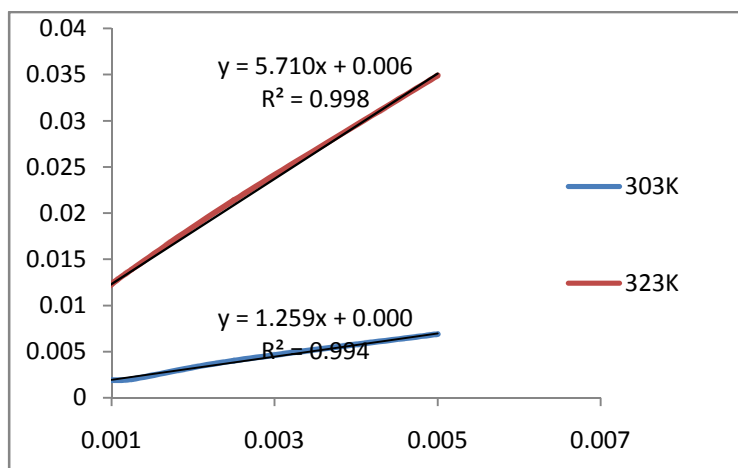
_____

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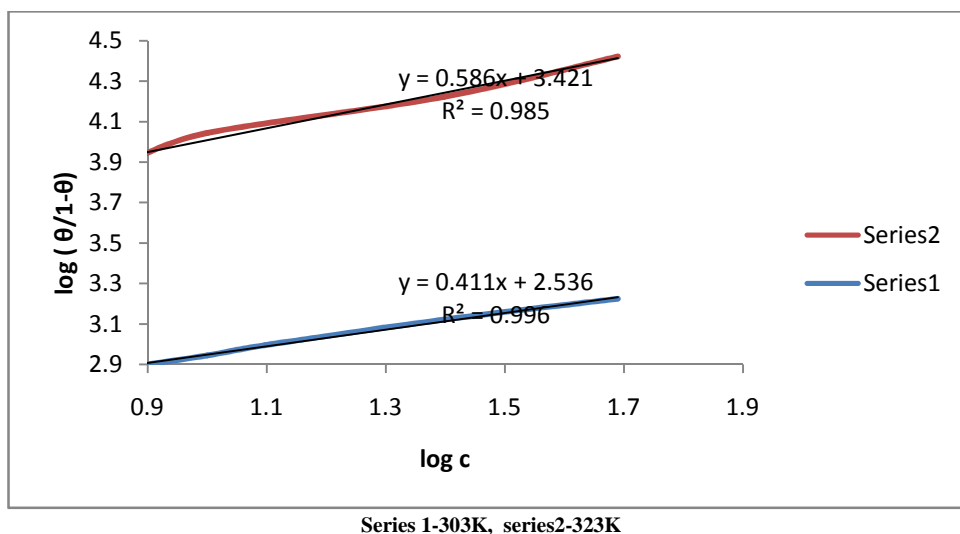

Series 1-303K, series2-323K

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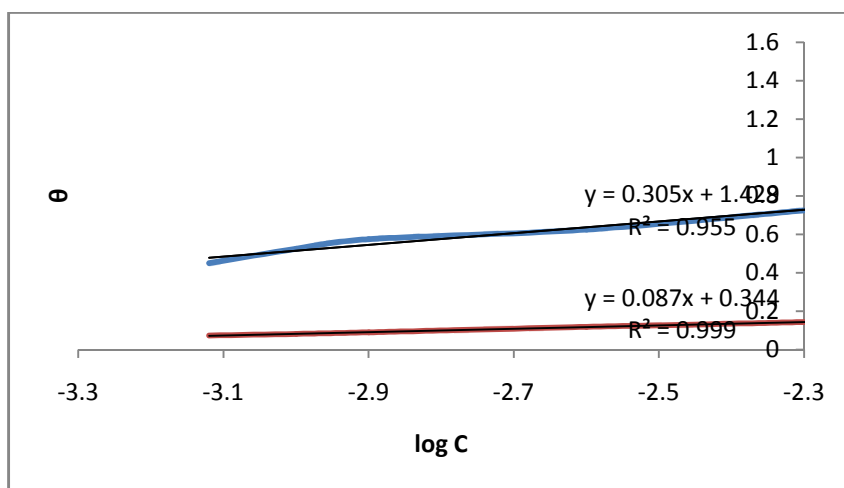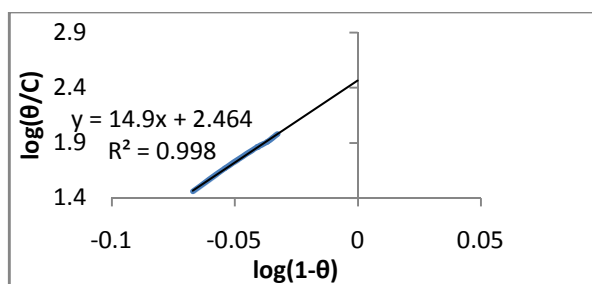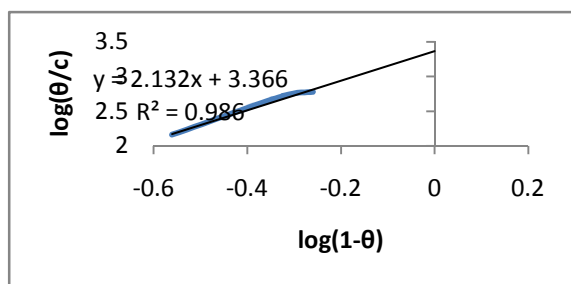

Fig.4. Flory-Huggins adsorption isotherm for HMPHPP in 1.0 N NaOH solutions

Fig.4a. at 303K   **Fig.4b. at 323**

Gasometric method

The degree of surface coverage and inhibition efficiency were calculated using the following formulas

$$\theta = \%I/100 \underline{\hspace{3cm}}(8)$$

$$\%I = \left\{1 - \frac{V'_{Ht}}{V^{\circ}_{Ht}}\right\} \times 100 \underline{\hspace{2cm}}(9)$$

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.

The variation of the volume of hydrogen gas evolved with time for the corrosion of aluminium in 1.0 N NaOH medium is shown (Fig.5) It is clear from the figure that the volume of the volume of hydrogen gas evolved decreases with increase in the concentration of HMPHPP indicating that the corrosion rate of aluminium is inhibited by HMPHPP in 1.0N NaOH [19, 20]. The calculated values are given (Table.3). There is good agreement between the %IE in weight loss and gasometric method.

Table: 3 Gasometric determination %IE

C, [M]	Volume of hydrogen, ml	% IE
Blank	78.5	
5×10^{-4}	26.8	65.9
5×10^{-3}	21.3	72.9

Fig.5.Volume of Hydrogen gas evolved with time
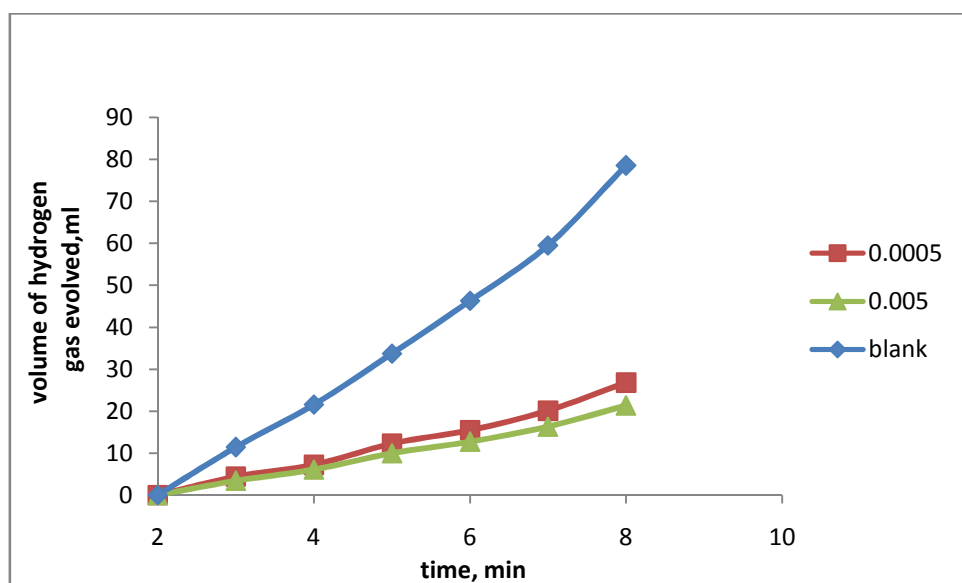
Synergistic effect:
The synergistic parameter S_θ was calculated by the following formula

$$S_\theta = (1 - \theta_{1+2})/(1 - \theta'_{1+2})_____(10)$$

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 increased the inhibition efficiency in the presence of HMPHPP in 1.0 N NaOH The inhibitor HMPHPP was observed to significantly inhibit the corrosion of aluminium in alkaline medium. The inhibition efficiency was further increased by the addition of 0.00075M tetrabutylammoniumbromide (TBAB) to each concentration of the inhibitor. The results are given (Table 4). It is clear the inhibition efficiency synergistically increases on addition of 0.00075M TBAB to different concentrations of HMPHPP.

Table 4: Corrosion parameters for aluminium in 0.1 N NaOH in the presence of HMPHPP + 0.00075M TBAB mixture

Concentration, M	%IE	S_θ
TBAB(0.00075)	9.0	
1×10^{-4}+TBAB	51.0	1.7
1.25×10^{-4}+TBAB	52.1	1.6
2.5×10^{-4}+TBAB	60.6	1.7
5×10^{-4}+TBAB	64.8	1.5
7.5×10^{-4}+TBAB	73.2	1.7

_____

Electrochemical methods
Potentiodynamic polarization method
The formula used for calculating %IE by electrochemical polarization method was

$$\%IE = \frac{I_0 - I_{inh}}{I_0} \times 100 \qquad \underline{\hspace{3cm}} (11)$$

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

The effect of addition of different concentration of HMPHPP on the cathodic and anodic polarization curves of aluminium in 1.0 N NaOH solution at 303K was studied. The polarization curves are shown in Fig.6. Corrosion parameters such as, E_{corr}, I_{corr}, b_c, b_a and percentage inhibition efficiency are shown (Table 5). It observed from the Tafel curve that the inhibitor was mixed type because they enhance the anodic and cathodic processes but the anode is more polarized when an external current was applied. The corrosion potential also slightly shifted towards positive direction on increasing the concentration of the inhibitor. The current density value decreases with increasing concentration of HMPHPP, indicates that inhibitor retards the dissolution of aluminium in 1.0 N NaOH and the degree of inhibition depends on the concentration.

Table 5: potentiodynamic polarization parameters for aluminium in 1.0 N NaOH at different concentration of HMPHPP

Concentration, M	$-E_{corr}$, V	I_{corr}, mV dec^{-1}	b_c, mV dec^{-1}	b_a mV dec^{-1}	% IE
Blank	1.592	16135.63	270.5	496.5	
7.5×10^{-4}	1.591	10660.00	188.1	597.5	33.9
1×10^{-3}	1.582	8422.55	185.3	607.7	47.8
1.25×10^{-3}	1.593	8162.69	181.1	577.6	49.4
2.5×10^{-3}	1.520	5981.82	210.8	607.7	62.3
5×10^{-3}	1.573	3925.99	176.1	491.0	75.7

Fig.6. Tafel plot
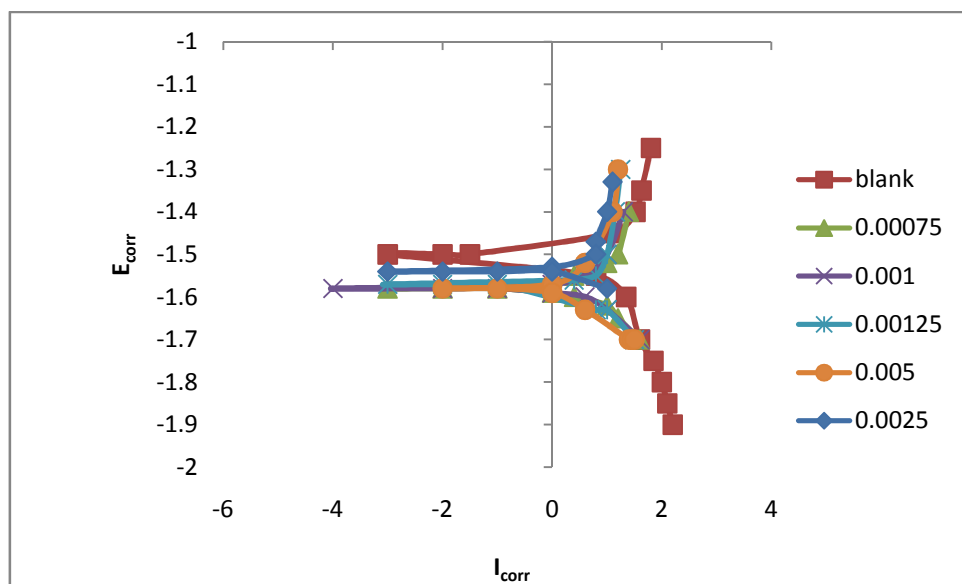
Impedance method
The corrosion behavior of aluminium in 1.0 N NaOH solution in absence and presence of inhibitor was also tested using electrochemical impedance spectroscopy (EIS).

The formula used for calculating %IE by EIS was

$$\%\text{IE}= \frac{R_{ct(inh)}-R_{ct}}{R_{ct(inh)}} \times 100 _____(12)$$

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

The calculated impedence parameters such as charge transfer resistance, double layer capacitance and percentage inhibition efficiency are given (Table 6). Nyquist plots of aluminium in 1.0 N NaOH, in the absence and presence of different concentrations of HMPHPP, are shown (Fig.7). It is apparent from these plots that the impedance in all cases corresponds to the capacitive diameter and it depends on the HMPHPP concentration and they increase with increasing of HMPHPP concentration. This indicates that the impedance of inhibited substrate increases with increasing inhibitor concentration and consequently the inhibition efficiency increases [22, 23]. The value of R_{ct} increases and C_{dl} decreases with the increase in concentration of HMPHPP indicating 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 HMPHPP on aluminium surface.

Table 6: EIS measurement parameters for different concentration of HMPHPP in alkaline medium

Concentration, M	R(ohm)	$C_{dl}\,(\mu F)$	%IE
Blank	0.9075	55.5	
7.5×10^{-4}	1.356	33.14	33.1
1×10^{-3}	1.985	37.24	54.3
1.25×10^{-3}	1.944	22.25	53.3
2.5×10^{-3}	2.700	-	66.4
5×10^{-3}	4.578	23.69	80.0

Fig.7. Nyquist plot
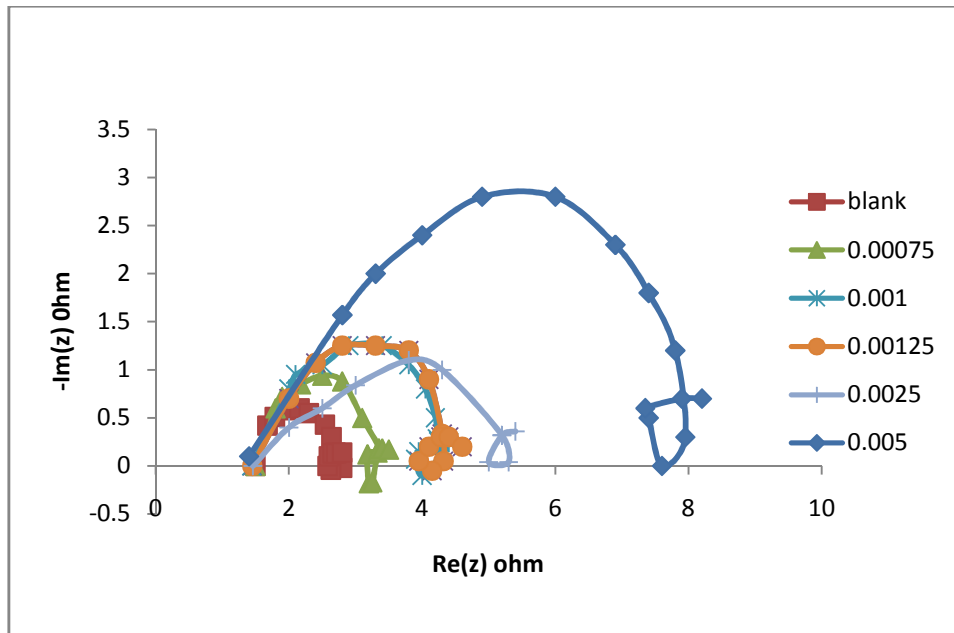
SEM Technique
Representative scanning electron micrographs (SEM) of aluminium surface in 1.0N NaOH solution with and without HMPHPP are shown (Fig.8a & 8b). The figure clearly indicates that the organic inhibitor covers the irregular cracks by the deposition of inhibitor molecule on it.

_____

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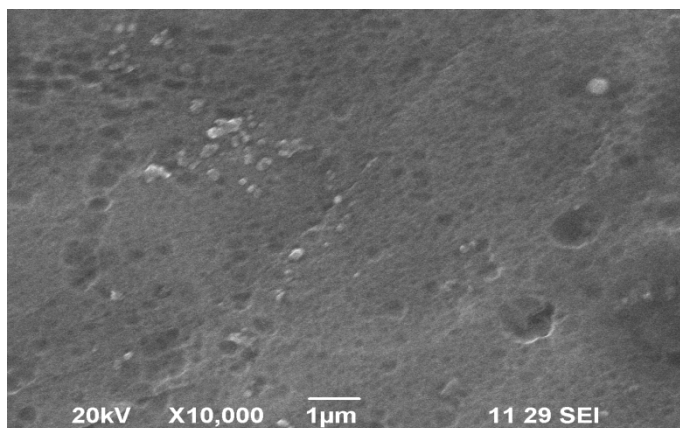

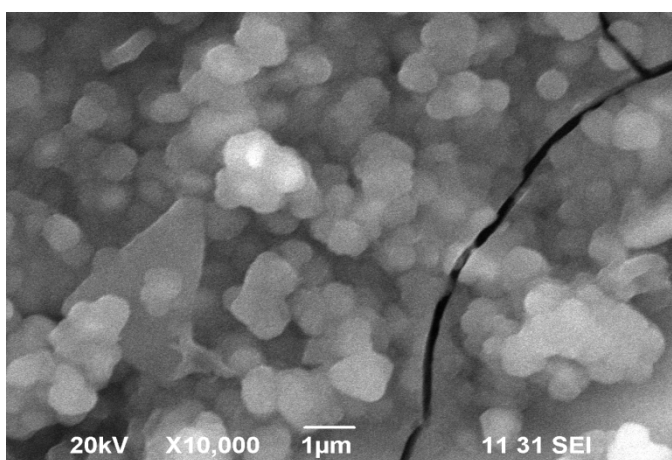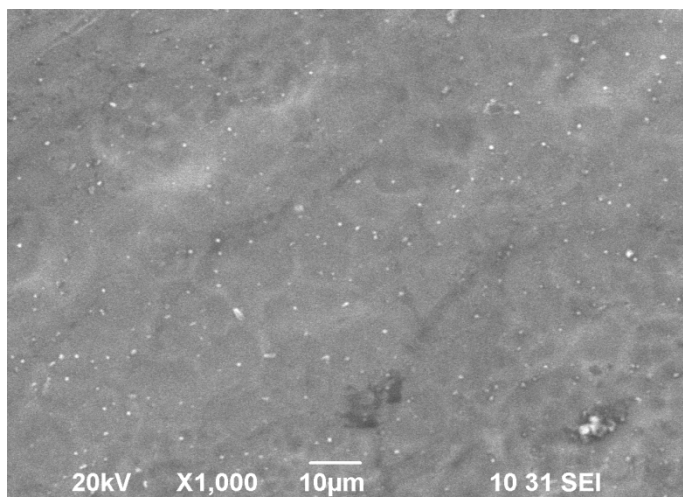**Fig.8b SEM photograph of aluminium after immersed in 1.0 N NaOH solution**

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

CONCLUSION

1. 3-(4-hydroxy-3-methoxy-phenyl)-1-(2-hydroxy-Phenyl-propenone (HMPHPP) showed a maximum of 72.5% 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 inhibitor by gasometric method

4. Addition of TBAB increases the inhibition efficiency of HMPPP.

---

5. The process of adsorption of the inhibitor obeys the entire four adsorption isotherm discussed.
6. The inhibitor was found to be of mixed type.
7. The mechanism of adsorption appears to be physisorption.

REFERENCES

[1] DA Jones, Principle and prevention of corrosion of Metal, (**1992**), 25.
[2] EJ.Simmons, *Corrosion*, (**1955**), 11, 255.
[3] J Ishwara Bhar; Vijaya Alva, *Indian Journal of Chemical Technology*, **2009**, Vol.16, pp228-233.
[4] MA Quraishi; MA W.Khan; M Ajmal, *Anti-corros. Methods and Materials*, **1996**, 43, 5.
[5] S Murlidharan; SV.Iyer, *Anti-corros. Methods and Materials*, **1997**, 44, 100.
[6] N AL-Andis; E Khamis; H Aboul Enicm, *Corros. Prev. Control*, **1995**, 51, 441.
[7] B Hammouti; A Aouniti; M Taleb; M Brighli, S Kertit, *Corrosion*; **1995**, 51, 441.
[8] N Silver; DW Boykin, *J.Org. chem*., **1970**, 35, 759-764.
[9] B Zhao; W –Q Lu; Z.-H.Zhou; Y.Wu, *J. Mater.Chem*., **2000**, 79, 1119-1121.
[10] SA Umoren; O Ogbobe; EE.Ebenso; UJ.Ekpe, *Pigments & Resin Tech*., **2006**, 35(5), 284.
[11] SA Umoren; EE Ebenso; PC Okafor; UJ Ekpe; O Oguzie, *Anto.Corros.Methods and Materials*, **2007**, 15(5), 2810.
[12] M Metikos-Hikovic; Z Grubac; Stupisek-E.Lisac, Corrs.
[13] EE Oguzie, *Corros. Sci*., **2007**, 49, 1529.
[14] ES Ferreira; C Giacomelli; FC Gicomelli; A Spinell, *Mater. Chem. Phys*., **2004**, 83(1), 129.
[15] A Popova; E Sokolova; S Raicheva; M Christov, *Corros. Sci.,* **2003**, 45, 33.
[16] KC Emregul; AA Akay; O Atakol, *Mater Chem. Phy*., **2005**, 93, 325-329.
[17] I Langmuir, *J. Am. Soc.,* 38, (**1916**), P.2221.
[18] Libin Tang; Xueming Li; YunsenSi; Guannan Mu; Guangheng Liu, *Mateer. Chem. Phys*, 95 (**2006**), 29.
[19] NO Eddy; AS Ekop. *J. Mater. Sci.,* 4(1), 10-16.
[20] NO Eddy; P Ekwumemgbo; SA Odoemelam, *International Journal of Physical Sciences*, **2008**, Vol.3 (11), PP.275-280.
[21] XY He; HY Deng; R Li; XD Fei; HY Wang; ZY Deng. *Acta Metal. Sin. (Engl. Lett.),* **2008**, Vol.21, No.1, pp65-71.
[22] DC Silverman, J.E.Carrico, *Corrosion* 44 (**1988**) 280.
[23] DC Silverman. *Corrosion*, 46, (**1990**), 589.
[24] A Zarrouk; B Hammout; H Zarrok; I Warad; M Bouachrine, *Der Pharma Chemica*, **2011**, 3(5), 263-271.
[25] NO Obi-Egbedi; KE Essien; IB Obot, *J.Comput. Method.Mol.Design*, **2011**, 1(1), 26-43.
[26] KM Omatola; IC Okeme, *Archieves of Applied Science Research*, **2012**.4(4), 1825-1832.
[27] M Khaled; Elsabawy; H Nader; Elbagoary; A Mohamed; A Moussa, *J. Comput. Method Mol. Design*, **2011**, 1(4), 46-56.