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Inhibition of the corrosion of aluminium in alkaline medium by 1-(phenyl)-3-(2-hydroxy phenyl)-propenone in the presence of tetrabutylammonium bromide

J. R. Beulah Thavamani Esther Rani^a and T. Jeyaraj^b

^aPG and Research Department of Chemistry, Bishop Heber College (Autonomous), Tiruchirapalli.(INDIA)

^bPG and Research Department of Chemistry, Jamal Mohammed College (Autonomous), Tiruchirapalli.(INDIA)

ABSTRACT

The inhibitive ,thermodynamics and adsorptive properties of 1-(phenyl)-3-(2-hydroxy phenyl)-propenone (PHPP) and tetrabutylammonium bromide (TBAB) for the corrosion of aluminium in 1.0 M NaOH solutions have been investigated by weight loss measurements at 303K and 323K and electrochemical measurements at 303K . It was found that the inhibition efficiency increased with PHPP concentration but decreased with increase in temperature. A synergistic effect was observed between TBAB and PHPP. The experimental results suggest that the presence of TBAB in the solutions stabilized the adsorption of PHPP molecules on the metal surfaces and therefore improve the inhibition efficiency. The mechanism of adsorption of inhibitors was proposed from the trend of inhibition efficiency with temperature and the values of E_a , ΔG_{ads} , Q_{ads} . Langmuir and Flory-Huggins adsorption isotherms were found to conform to the adsorption of the inhibitor on the aluminium surface in 1.0 M NaOH.

Keywords: Corrosion inhibition, physical adsorption, synergism parameter, adsorption isotherm and charge transfer resistance.

INTRODUCTION

Aluminum is the third most abundant element. The use of aluminium in the energy field is its application in batteries. With strongly alkaline electrolyte (p^H 14), the potential for the discharge of pure aluminium can be as low as -2.33V; with respect to the standard hydrogen electrode [1] .The tri-valence of aluminium along with its light weight yields a high electrochemical equivalence of 2.984h/g [2]. Thus aluminium is a suitable anode material for hundreds of years. Eventhough, aluminium act as anode, in alkaline medium it undergoes corrosion with hydrogen evolution. In the efforts to mitigate aluminium corrosion, the main strategy is to effectively isolate the metal from corrosive agents, by the use of corrosion inhibitors. Organic substances containing polar functions with nitrogen, oxygen and/or sulphur atoms in a conjugated system have been reported to exhibit good inhibiting properties. Corrosion inhibition occurs via adsorption of their molecules on the corroding metal surface and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under

particular conditions [3]. The inhibitor used in the present study (PHPP) 1-(phenyl)-3-(2-hydroxy phenyl)-propenone is a non toxic, and environmental friendly organic compound. It contains O atoms containing lone pairs of electrons as act as active centres and aromatic rings with delocalize π electrons which could aid its adsorption onto metal surfaces. Furthermore it has a high molecular weight (224) and likely to cover more surface area (due to adsorption) of the metal thus effectively preventing corrosion from taking place [4]. The present study aims at investigating the inhibitive effect of PHPP on aluminium corrosion in alkaline medium under various temperatures (303K and 323K using weight loss method and electrochemical methods). The influence of TBAB on the adsorption and corrosion inhibitive properties of PHPP has also been studied.

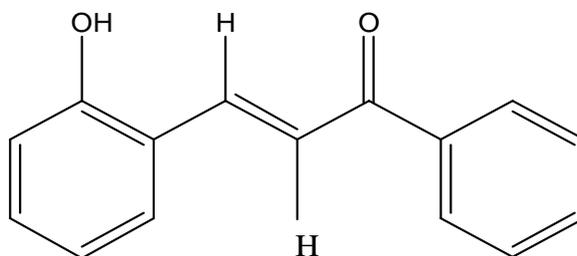
MATERIALS AND METHODS

Materials preparations

Commercially available aluminium sheet was cut to form different coupons of dimension, 2.0 cm x 1.0 cm x 0.14 cm for weight loss studies. Each coupon was washed with ethanol, rinsed with acetone and allowed to dry in the air before preservation in the desiccators. The aluminium specimens for the electrochemical measurements were machine cut from aluminium sample into test electrodes of dimensions, 8 cm x 1 cm x 0.14 cm and coated with epoxy resin (araldite) leaving a surface area of 1cm^2 . All reagents used for the study were analytical grade and double distilled water was used for the study.

Synthesis of 1-(phenyl)-3-(2-hydroxy phenyl)-propenone (PHPP)

The compound, 1-(phenyl)-3-(2-hydroxy phenyl)-propenone was synthesized and recrystallised as per the reported procedure detailed below [5]. A mixture of O-hydroxybenzaldehyde (0.43mol), Acetophenone (0.43mol) and sodium hydroxide (0.55 mol) in ethanol was stirred continuously with mechanical stirrer at room temperature for about 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 recrystallised from ethanol and it was characterized by uv-visible and I.R spectral studies. The molecular weight of the compound (224) was determined by Rast method of determining molecular weight and the value was found to agree with formula weight. The structure of the molecule is shown below. The inhibitor, PHPP was dissolved in 1.0 M sodium hydroxide in appropriate quantities for the inhibition studies.



1-(phenyl)-3-(2-hydroxy phenyl)-propenone (PHPP)

Gravimetric experiment:

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

Electrochemical measurements

The aluminium coupons, prepared as detailed above, was 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 of aluminium as working electrode (WE), platinum as counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. The electrode potential was allowed to stabilize for 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 -1.3 mV around open circuit potential with scan rate of 10 mV/sec. Impedance measurements were carried out in frequency range from 10 kHz to 1 Hz using ac signals with an amplitude of 27 mV peak to peak at open circuit potential.

RESULTS AND DISCUSSION

The inhibition efficiency of the inhibitor (%I) and degree of surface coverage (θ) were determined from the weight loss data using equations 1 and 2 respectively.

$$\%IE = \left(1 - \frac{W_2}{W_1}\right) \times 100 \quad (1)$$

$$\Theta = \left(1 - \frac{W_2}{W_1}\right) \quad (2)$$

where W_1 and W_2 are weight losses of aluminium in the absence and in the presence of inhibitor. The variation of weight loss for the corrosion of aluminium in 1M NaOH, in the absence and presence of various concentrations of the inhibitor at 303K and 323K was determined. The results were recorded in Table 1.

Table 1: Corrosion parameters for aluminium in 1M NaOH in the absence and presence of different concentrations of (PHPP) at 303K and 323K.

[Inhibitor],M	Θ , Temperature		(IE %)	
	303K	323K	303K	323K
0.000025	0.090	-	9.00	-
0.000050	0.143	-	14.3	-
0.000075	0.200	-	20.0	-
0.000100	0.371	-	37.1	-
0.000250	0.580	0.492	58.0	49.2
0.000500	0.630	-	63.0	-
0.000750	0.650	-	65.0	-
0.002500	0.710	0.69	71.0	69
0.005000	0.730	0.70	73.0	70
0.007500	0.745	0.73	74.5	73
0.010000	0.760	0.74	76.0	74

The results revealed that the inhibition efficiencies increased with increase in concentrations of PHPP and decreased with increasing temperature, indicating that the adsorption of (PHPP) on Aluminium surface is consistent with the mechanism of physical adsorption [6-12].

Adsorption consideration

It has been suggested generally that physically adsorbed molecules are attached to the metal at the cathodes and essentially retard metal dissolution by inhibiting the cathodic reaction whereas chemically adsorbed molecules protect anodic areas and reduce the dissolution of the metal at the sites where they are attached [13-15]. The nature of adsorption, has been assessed using the values of surface coverage (θ) for the system at two different temperature 303K and 323K. By fitting θ values to the isotherms of Frumkin, Langmuir, Flory-Huggins, Temkin and El-Awady's et al. The correlation coefficient (R^2) values were used to determine the best fit isotherm.

Langmuir adsorption isotherm model has the form,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

where θ is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process.

The slope deviates from unity indicating that there is attraction or repulsion in the adsorbed layer of the inhibitor on the aluminium surface. [16, 17].

The Flory-Huggins adsorption isotherm can be given by the following equation [4]

$$\log\left(\frac{\theta}{C}\right) = \log K + \log(1-\theta) \quad (4)$$

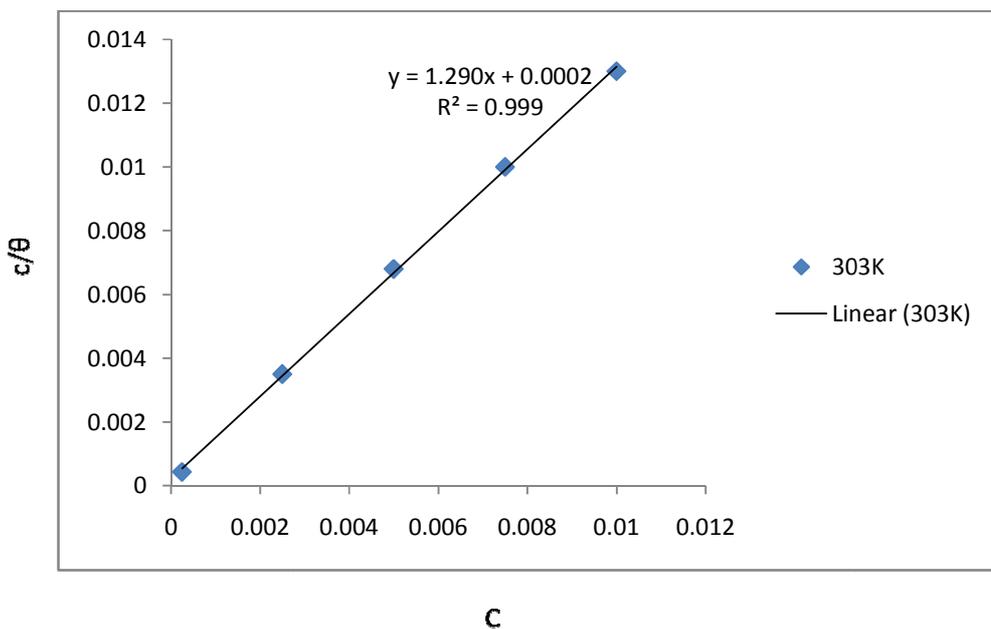


Figure 1.

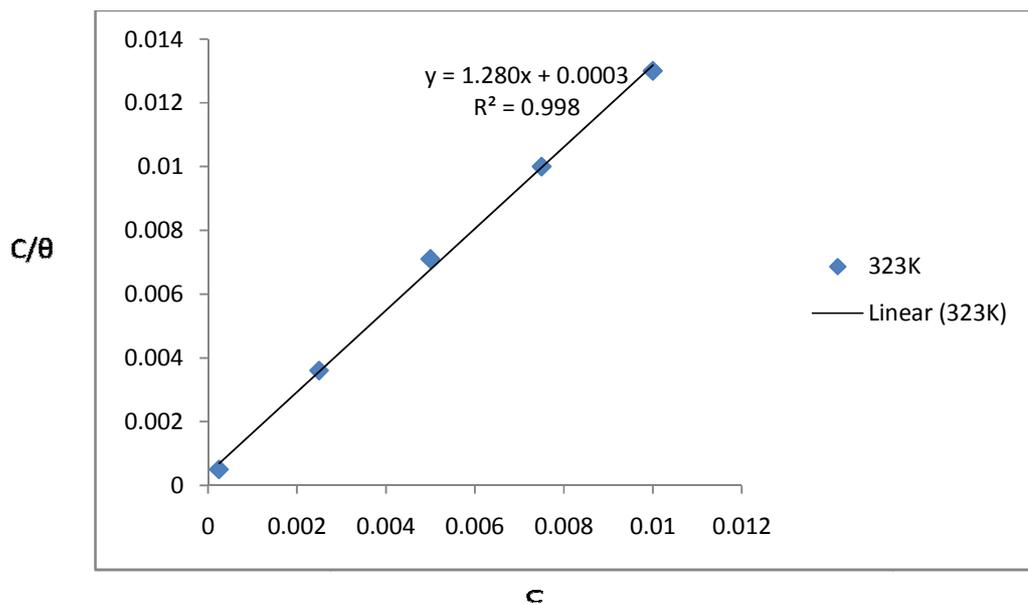


Figure 2.

The plots of $\log\left(\frac{\theta}{c}\right)$ against $\log(1-\theta)$ gave a linear relationship (fig.3 and fig.4) showing that Flory-Huggins isotherm was obeyed. The values of the size parameter(x) are positive (Table 2).It indicates that the PHPP inhibitor molecules are adsorbed on aluminium surface by displacing more than one water molecule [12].

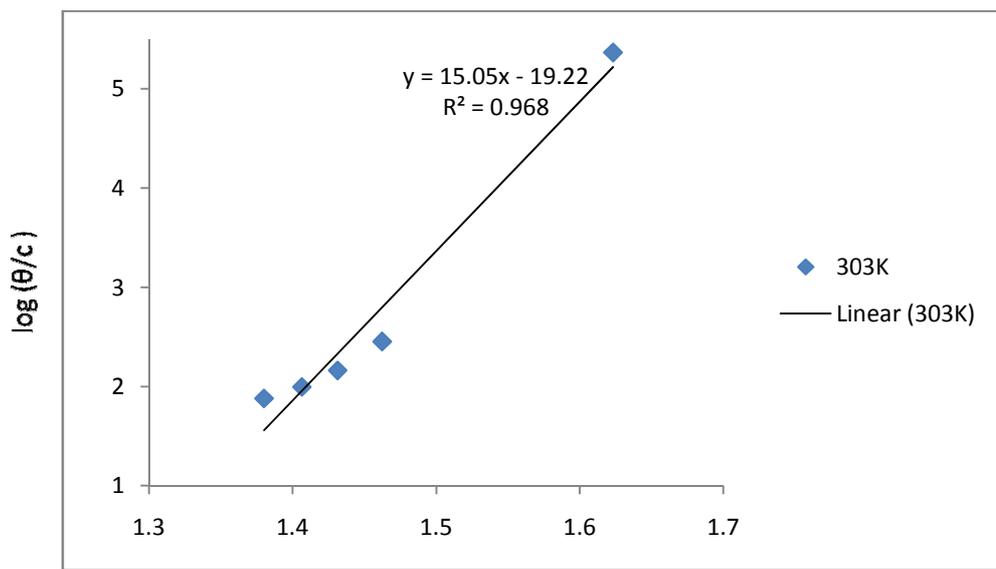


Figure 3.

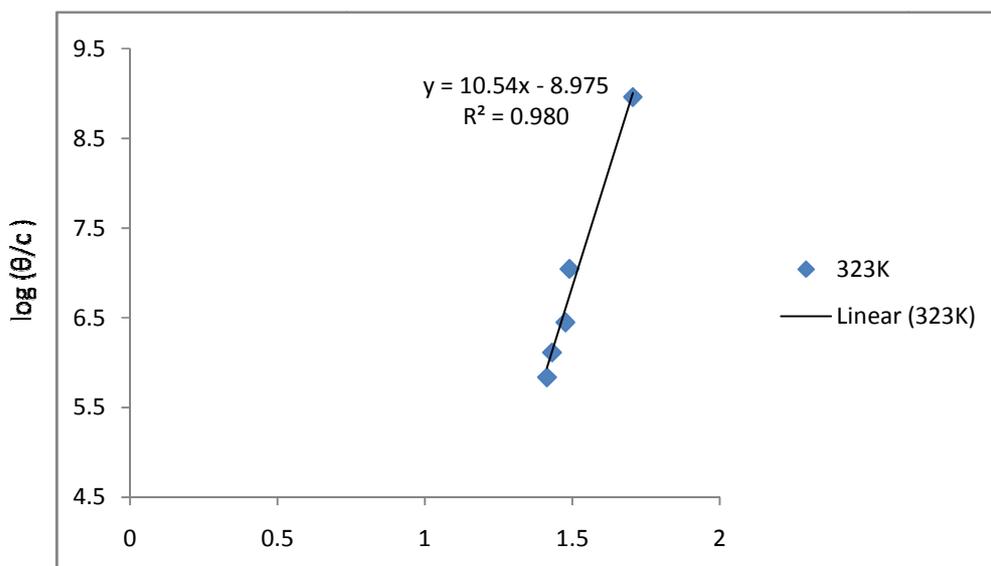


Figure 4.

Table 2: Adsorption parameters of different isotherms on aluminium surface.

Isotherms	Temperature	R^2	$\text{Log}K_{ads}$	x	$\Delta G_{ads}^\circ, \text{kJmol}^{-1}$
Langmuir	30°C	0.999	3.674	-	-31.436
	50°C	0.998	3.522	-	-30.559
Flory-Huggins	30°C	0.968	-1.2766	15.05	-17.523
	50°C	0.980	-0.8338	10.25	-5.283

Kinetic and thermodynamic consideration

The inhibitor adsorption mechanism was further elucidating by the kinetic assessment of the experimental data. The apparent activation energies (E_a) for the corrosion process, in the absence and in the presence of inhibitor were evaluated from Arrhenius equation, which is given below [18,19].

$$\log \frac{r_2}{r_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5)$$

where r_1 and r_2 are the corrosion rates at temperature 303K and 323K, respectively. The heat of adsorption, Q_{ads} , was calculated using the following equation [20-23].

$$Q_{ads} = 2.303R \left[\log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right] \times \left[\frac{T_1 T_2}{T_2 - T_1} \right] \text{ kJ mol}^{-1} \quad (6)$$

where R is the gas constant, θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2 respectively. The E_a values and Q_{ads} were calculated using equations (8) and (9), are presented in Table 3.

Table 3. Calculated values of E_a and Q_{ads} for the dissolution of aluminium dissolution in 1.0 M NaOH without and with PHPP

[inhibitor], M	E_a , kJ mol^{-1}	Q_{ads} , kJ mol^{-1}
Blank	3.687	--
0.00025	4.542	-14.437
0.00250	3.895	-3.869
0.00500	4.070	-6.001
0.00750	3.918	-3.153
0.01000	4.123	-4.344

E_a values ranged from 3.895 to 4.542 kJ mol^{-1} and are lower than the threshold value of 80 kJ mol^{-1} required for chemical adsorption, indicating that the adsorption of (PHPP) on aluminium surface occurs by the mechanism of physical adsorption [24, 25]. The heat of adsorption Q_{ads} values were negative and ranged from -3.153 to -14.437 kJ mol^{-1} indicating that the adsorption of (PHPP) on aluminium surface is exothermic and the inhibition efficiency decreased with rise in temperature and it also support the physical adsorption mechanism [26,27].

Effect of tetrabutylammonium bromide addition

Literature survey reported that the presence of quaternary compounds in alkaline media yields an excellent inhibition efficiency [28]. It is observed that the TBAB improves adsorption efficiency of the organic inhibitor (PHPP) by forming intermediate bridges between the metal surface and the organic inhibitor. The observed enhancement of inhibition efficiency of PHPP, in the presence of TBAB ions, was determined by the synergism parameter S_θ , was evaluated using the relationship given by Armaki and Hackerman [29]:

$$S_\theta = \frac{1-\theta_{1+2}}{1-\theta_{1+2}} \quad (7)$$

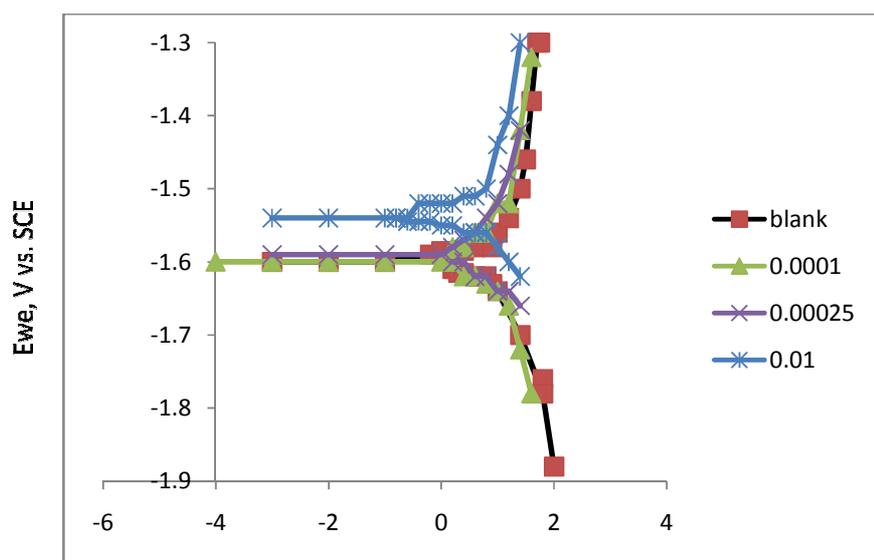
where $\theta_{1+2} = (\theta_1 + \theta_2)$; θ_1 surface area coverage of the TBA^+ cation, θ_2 surface area coverage of the organic anion and θ^* = measured inhibition efficiency for the organic inhibitor anion in combination with TBA cation. The results obtained are presented (Table 4). The S_θ values are greater than unity, suggesting that the enhanced inhibition efficiency, resulting from the combination of organic inhibitor anion and TBA^+ cation is due to synergism. Similar results have been reported [30].

Table 4 Synergistic parameter S_{θ} values for different concentrations of PHPP determined from weight loss method at 303K

[Inhibitor],M	Surface area coverage, θ	Inhibition efficiency (%I)	Synergism parameter S_{θ}
TBAB			
0.00075	0.094	9.4	-
PHPP			
0.000075	0.200	20.0	-
0.000100	0.371	37.1	-
0.000250	0.580	58.0	-
0.000500	0.630	63.0	-
0.000750	0.650	65.0	-
TBAB+PHPP			
0.00075+0.000075	0.580	58.0	1.68
0.00075+0.000100	0.560	56.0	1.22
0.00075+0.000250	0.760	76.0	1.36
0.00075+0.000500	0.730	73.0	1.02
0.00075+0.000750	0.790	79.0	1.22

Potentiodynamic polarization measurements

The potentiodynamic polarization curves (fig.5 and 6) for aluminium in 1M NaOH with and without the addition of PHPP in various concentrations.



Log I (mA Cm⁻²)

Figure 5.

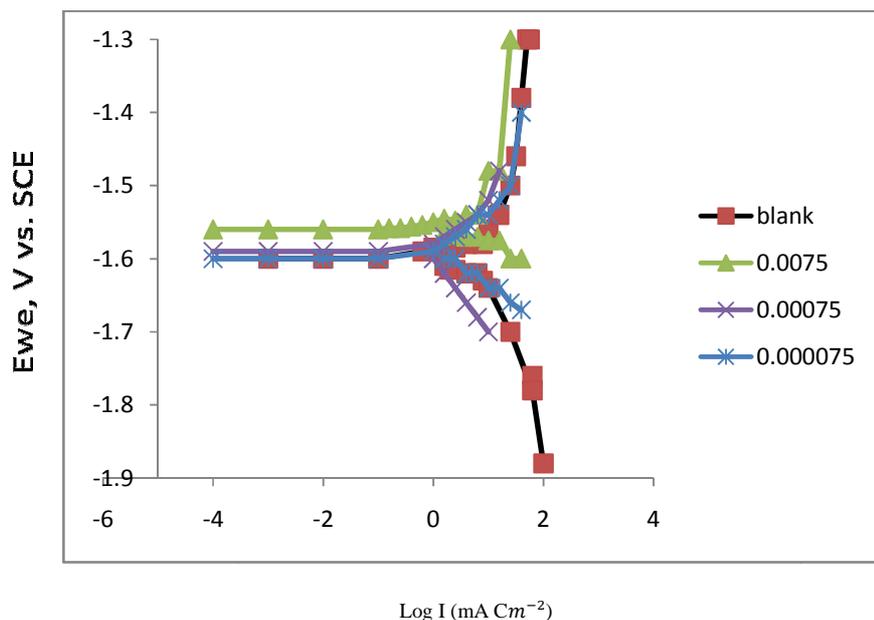


Figure 6.

The corrosion potential (E_{corr}), corrosion current density (i_{corr}) anodic and cathodic slopes (β_a and β_c) at different inhibitor concentrations are shown (Table 3).

Table 3: The electrochemical parameters for the corrosion of aluminium in 1M NaOH in the absence and presence of different concentration of PHPP at 303K.

[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
7.50 x 10 ⁻⁵	-1.583	13.599	273.6	489.5
1.00 x 10 ⁻⁴	-1.579	12.540	277.5	492.3
2.50 x 10 ⁻⁴	-1.574	9.313	257.0	523.3
7.50 x 10 ⁻⁴	-1.566	10.211	262.3	533.5
7.50 x 10 ⁻³	-1.544	8.077	222.4	438.6
1.00 x 10 ⁻²	-1.533	6.448	222.1	394.3

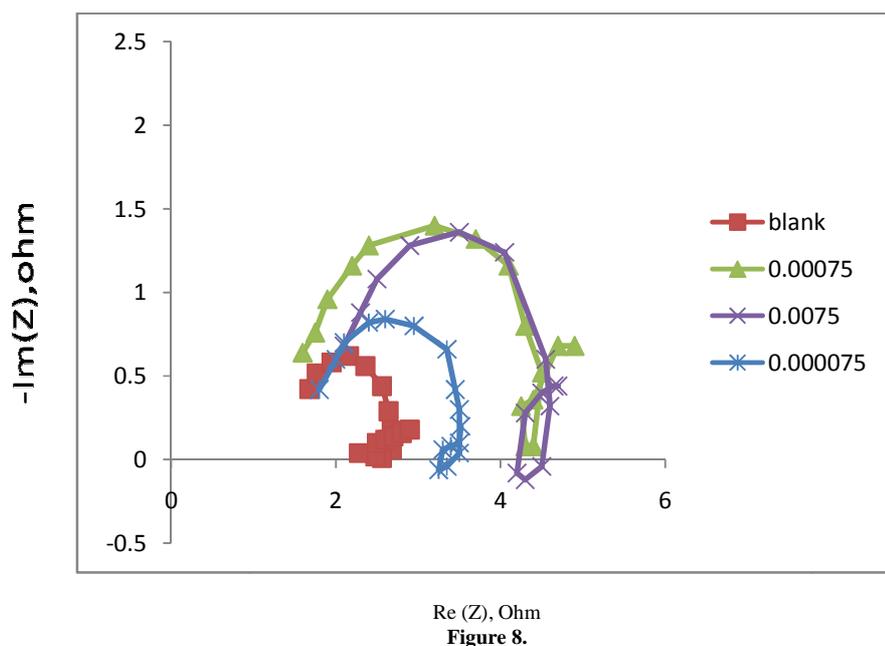
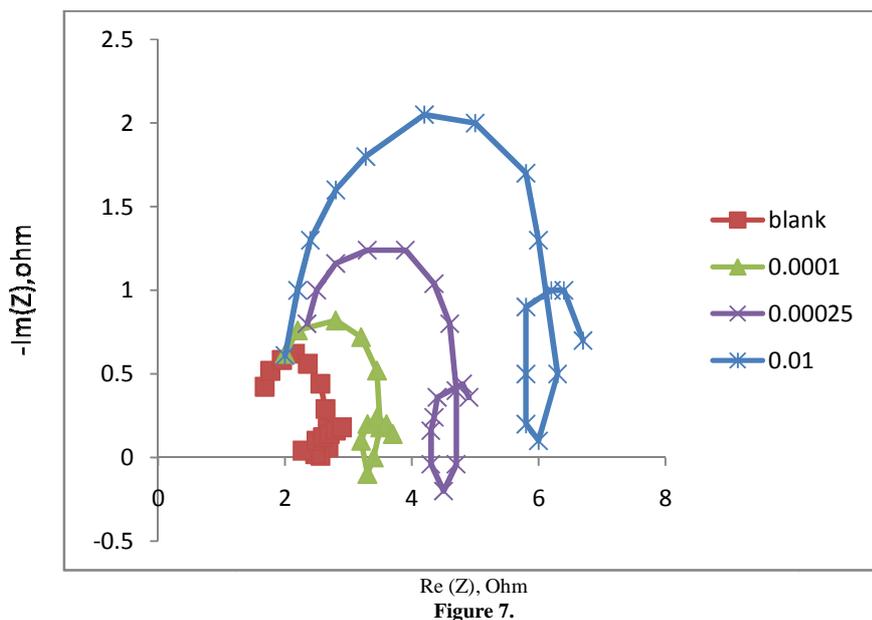
Both the anodic and cathodic Tafel slopes were altered significantly and it suggested that the inhibitor exerted an efficient inhibitory effect both on anodic dissolution of metal and on cathodic hydrogen reduction reaction[31]. The corrosion potential is shifted to positive direction at most by +59 mV and the corrosion current decreases markedly [32, 33]. These results indicate that the inhibitor acts as a mixed type indicator.

Electrochemical impedance measurements

The effects of the inhibitor concentration on the impedance behaviour of the aluminium in NaOH were studied. Nyquist plots of aluminium in 1M NaOH in the presence and absence of various concentrations of PHPP are given (fig.7). The inhibition efficiency, (%IE) were calculated from the impedance data by applying the following relationship:

$$\%IE = \frac{R_p - R_{p0}}{R_p} \times 100 \tag{8}$$

Where R_{p0} and R_p are the polarization resistance in the absence and presence of PHPP.



The impedance diagram consists of a large capacitive loop which is semicircle in shape at high frequencies and a small inductive one at the medium frequencies. The semicircle loop indicates that a charge transfer process mainly controls the corrosion of aluminium. Deviations of perfect circular shape can be inferred as the frequency dispersion of interfacial impedance. This is due to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena [34, 35]. The impedance parameters derived from investigations are given in Table 4.

Table 4 Impedance parameters for the corrosion of aluminium in 1M NaOH in the absence and presence of different concentration of PHPP at 303K.

Concentrations	R_p , ohm	C_{dl} , μF	%IE
Blank	0.9075	55.5	-
7.50×10^{-5}	1.476	49.26	38
1.00×10^{-4}	1.300	56.83	30.3
2.50×10^{-4}	1.987	37.19	54.70
7.50×10^{-4}	2.283	47.51	60.35
7.50×10^{-3}	2.829	-	68.00
1.00×10^{-2}	3.966	58.06	77.18

The effective corrosion resistance is observed due to the increase of R_p and the decrease of C_{dl} values [36].

CONCLUSION

The chalcone PHPP was used as a inhibitor for aluminium corrosion in alkaline media. The inhibition efficiency (%I) increased with increasing inhibitor concentration. The inhibition efficiency decreased with increasing temperature indicating a weak interaction between the inhibitor molecules and the aluminium surface. Polarisation studies reveals that the inhibitors act as a mixed type indicator. The values of R_p increased while the C_{dl} values decreased with the addition of inhibitor indicating the formation of a surface film. The TBAB shows synergism with PHPP. The inhibition efficiency obtained from chemical method and electrochemical method are in the same trend.

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REFERENCES

- [1]. Rand DAJ, Woods R, Dell RM, Batteries for electric vehicles, Somerset Research studies press Ltd, **1998**.
- [2]. Li, Bjerrum NJ, J power sources **2002**, 110,1.
- [3]. La Nnanna, Anozie IU, Avoaja AGI, Akoma CS, Eti EP, *African Journal of pure and Applied chemistry*, **2011**, 5, 265.
- [4]. obot IB, obi-Egbedi No, Umoren SA, *Der Pharmachemica*, **2009**, 1,151.
- [5]. Ahluwalia VK, Pooja Bhagat , Renu Aggarwal, Ramesh Chandra , Intermediates for Organic Synthesis , I.K.Intrenational Pvt . LTd ,New Delhi,**2005**,pp 336.
- [6]. Odiongenyi AO, Odoemelam SA, Eddy NO, *Portugalia Electrochem Acta*, **2009**, 27,33.
- [7]. EddyNO, Ibok UJ, Ebenso EE, El Nemr A, Ashry El, el SH ,*J.mol.Model*, **2009**, 15,1085.
- [8]. Eddy NO, Odeomelam SA, *Resin pigment Technol*, **2009**, 38,111.
- [9]. Eddy NO, Mamza PAP, *Portugalia Electrochem. Acta*, **2009**, 27,443.
- [10]. Ebenso EE, *Bull of Electrochem*,**2003**, 19,209.
- [11]. Ebenso EE, *Mat. Chem. Pys.* **2003**, 79,58.
- [12]. Abdallah M, *Corros.Sci*, **2004**, 46,1981.
- [13]. Oguzie E, *Matter.Lett*, **2003**, 59 ,1076.
- [14]. Ebenso E, *Mater.Chem.phys*, **2003**, 79,58.
- [15]. Popova A, Sokolova E, Raicheva S, Christov M, *corros.sci*, 45,33.
- [16]. Migahed MA, Mohammed HM, Al-sabagh AM, *Mater.chem.phys*, **2003**,80,169.
- [17]. Durnie W, Marco RD, Jefferson A, Kinsella B, *J.Electrochem.soc*, **1999**,146,1751.
- [18]. Umasankareswari T, Jeyaraj T, *Der chemica sinica*, **2012**, 3, 1252.
- [19]. Iroha NB, Akaranta O, James AO, *Der chemica sinica*, **2012**, 3, 995.
- [20]. Eddy NO, Odoemelam SA, *J.Surface sc. Technol*, **2008**, 24, 1.
- [21]. Haiwala HM, Vashi RT, *Bull.Electrochem*,**2001**, 17, 441.
- [22]. Umoren SA, Ogbobe O, Ebenso EE, Ekpe UJ, *Resin Technol*, **2006**, 35,284.
- [23]. Umoren SA, Ebenso EE, Okafor PC, Ekpe UJ, Ogbobe O, *J.Appl.Polymer Sci*, **2006**, 103,2810.
- [24]. NO.Eddy and EE Ebenso, *African J pure Appl.chem*,**2008**, 2(6): 046-054.
- [25]. Eddy NO, Ekop AS, *J.mater sci*,**2008**, 4,10.
- [26]. Bhajiwala HM, Vashi RT, *Bull-Electrochem*, **2001**, 17, 441.
- [27]. Meenalochani G, Jeyaraj T, C Raja C , Ramya S, *Transanctions of the SAEST*, **2001**, 36, 3.

- [28]. Ebenso EE, *Mater.Chem. and Phys*, **2003**, 79, 58.
- [29].Abiola OK, *corros.Sci*, **2006**, 48, 3078.
- [30]. Ambrishsing, Eno E. Ebenso, QuraishiMA, *Int.J.Electrochem.sci*, **2012**, 7, 3409-3419.
- [31]. Ferreira ES, GilacomelliFC, Aspinelli, *Mater.Chem.Phys*, **2004**, 83, 129.
- [32]. Li, WH, He, Pei, CL, Hou, BR, *J.Appl. Electrochem*, **2008**, 38, 289.
- [33]. Da Costa SLFA, Agostinho SML, *Corros. Sci*, **1989**, 45, 472.
- [34]. Shih H, Mansfeld H, *Corros.Sci*, **1989**, 29, 2271.
- [35]. Yagan A, No Permez, Yildiz A, *Prog.org coatings*, **2006**, 57,314.
- [36].Lakshmiprabha K, Shameela Rajam,VenkatraRaman BR,*Der chemical sinica*,**2012**,3,114.