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A study of the use of 1-(4-hydroxyphenyl)-3-(2-hydroxyphenyl)-propenone as an inhibitor for the corrosion of aluminium in NaOH solution

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ABSTRACT

The present work is the investigation of the influence of 1-(4-hydroxyphenyl)-3-(2-hydroxyphenyl)-propenone on the corrosion behaviour of aluminium in 1.0 M NaOH solution by weight loss (at 30°C and 50°C), gasometric and electrochemical techniques. Experimental results revealed that inhibition efficiency increases with increasing inhibitor concentration up to a maximum of 77.5% and it decreased with increase of temperature. The best fit adsorption isotherm for the experimental data was Langmuir adsorption isotherm model at the studied temperatures. The mechanism of physical adsorption is proposed from the values of E_a , Q_{ads} and ΔG_{ads} . Tafel polarization analysis revealed that the studied compound is mixed type inhibitor. The data obtained from polarization studies, weight loss measurement and gasometric technique were in good agreement.

Keywords: Aluminium, corrosion, inhibition, adsorption, polarization.

INTRODUCTION

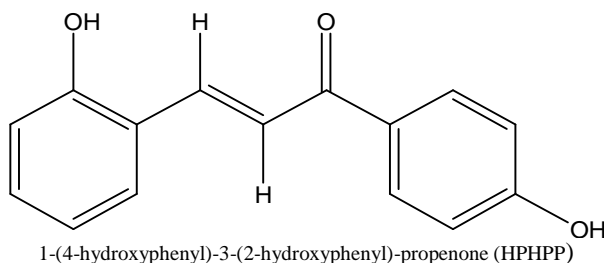
Aluminium from thermodynamic considerations is a very active metal. When oxygen is present (in the air, soil or water) aluminium instantly reacts to form aluminium oxide layer over the bare metal surface [1]. The oxide layer is compact, adherent and essentially inert to prevent corrosion. If the oxide film is damaged by a scratch, new oxide will immediately form on the bare aluminium metal [2]. Aluminium acts as anode material for high energy density power sources because of its attractive properties like highly negative potential and high theoretical energy density in alkaline media [3]. Further the aluminium/air battery is eco-friendly. However it is not greatly used in practice due to severe hydrogen evolution problems resulting from corrosion of the aluminium electrode. Mitigation of aluminium corrosion can be achieved using corrosion inhibitors. The corrosion behaviour of pure aluminium in alkaline solutions has been extensively studied in the development of the aluminium anode for the aluminium/air battery [4-7]. Most of the effective organic inhibitors used in industry have heteroatoms such as O, N, S containing multiple bonds in their molecules through which they can adsorb on the metal surface [8-11]. The chalcone inhibitor used in the study has O-atoms, C=C and phenyl rings and therefore it is expected to effectively inhibit the corrosion of commercial aluminium in 1.0 M NaOH.

MATERIALS AND METHODS

Specimens used in the weight loss experiment were mechanically cut from commercially available aluminium sample into coupons of 2.0 cm x 1.0 cm x 0.14 cm dimensions polished with soft 3M 1500 sand paper to a metallic shine, washed with acetone and double distilled water, dried to room temperature and stored in a moisture free desiccator before use in corrosion studies. 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 1 cm². The corrosive medium, 1.0 M NaOH solution was prepared from analytical reagent grade NaOH (MERCK) dissolved in double distilled water.

Synthesis of 1-(4-hydroxyphenyl)-3-(2-hydroxyphenyl)-propenone (HPHPP)

The compound, 1-(4-hydroxyphenyl)-3-(2-hydroxyphenyl)-propenone was synthesized and recrystallised as per the reported solvent-free synthesis procedure detailed below [12]. A mixture of *o*-hydroxybenzaldehyde (0.43 mol) and 4-hydroxyacetophenone (0.43 mol) and sodium hydroxide (0.55 mol) was ground by pestle in a mortar at room temperature for 5 minutes. The precipitated product was recrystallised from ethanol and it was identified by U.V and I.R spectra. The molecular weight of the compound (240) was confirmed by Rast method of determining molecular weight. The structure of the molecule is shown below. The HPHPP was dissolved in 1.0 M sodium hydroxide in appropriate quantities for the inhibition studies.



Weight loss measurements

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.

Gasometric method

The gasometric assembly is essentially an apparatus that measures the volume of gas evolved from a corrosion reaction system. It consists of essentially a two-necked round-bottom flask that serves as the reaction medium containing the corrodent and the metal coupons. Other parts are a separating funnel, a burette fitted with taps, and an outer glass jacket that serves as a water condenser. In monitoring corrosion studies using this technique, 100 ml of the corrodent 1M NaOH was introduced into the two-necked flask and the initial volume of air in the burette was noted. Thereafter, an aluminium coupon weighed approximately 2g was dropped into the corrodent and the flask was quickly closed. The volume of hydrogen gas evolved from the corrosion reaction was monitored by volume changes in the level of water in the graduated burette at fixed time intervals [13].

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 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 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 -1.1 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 an amplitude of 27 mV peak to peak at open circuit potential.

RESULTS AND DISCUSSION

Weight loss measurement and adsorption

The inhibition efficiencies, (I %) were calculated by the following equation.

$$I\% = \frac{w_0 - w_i}{w_0} \times 100 \tag{1}$$

where, W_0 and W_i are the weight losses in the absence and in the presence of the inhibitor respectively. The inhibition efficiency increases with increasing concentration of the inhibitor and decreased with increase of temperature (Table 1).

Table I Inhibition of corrosion of aluminium in 1.0 M NaOH by HPHPP at 30±0.5 and 50±0.5°C.

[Concentration] X 10 ⁻³ ,M	30°C		50°C	
	$\frac{W_0 - W_i}{W_0}$	%IE	$\frac{W_0 - W_i}{W_0}$	%IE
1.00	0.425	42.5	0.16	16.0
1.25	0.500	50.0	0.32	32.0
2.50	0.700	70.0	0.38	38.0
5.00	0.750	75.0	0.46	46.0
7.50	0.775	77.5	0.49	49.0

Adsorption of HPHPP can be explained on the basis that adsorption of the inhibitor was mainly via heteroatoms (viz, O) present in HPHPP in addition to the availability of π electrons in C=C and the aromatic system [12]. The establishment of isotherms that describe the adsorptive behaviour of a corrosion inhibitor is an important part of its study, as they can provide important clues to the nature of the metal-inhibitor interaction. The values of surface coverage (θ) are obtained from weight loss measurements at 30 and 50°C. The θ values were fitted to several adsorption isotherms and the best fit was found to obey Langmuir adsorption isotherm [14,] which is expressed by

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{2}$$

Where θ is the surface coverage, C is the inhibitor concentration and K_{ads} is the equilibrium constant of adsorption process. The regression coefficient, R^2 was found to be 0.996 (30°C) and 0.948 (50°C). Plot of C/ θ versus C is shown (Fig.1).

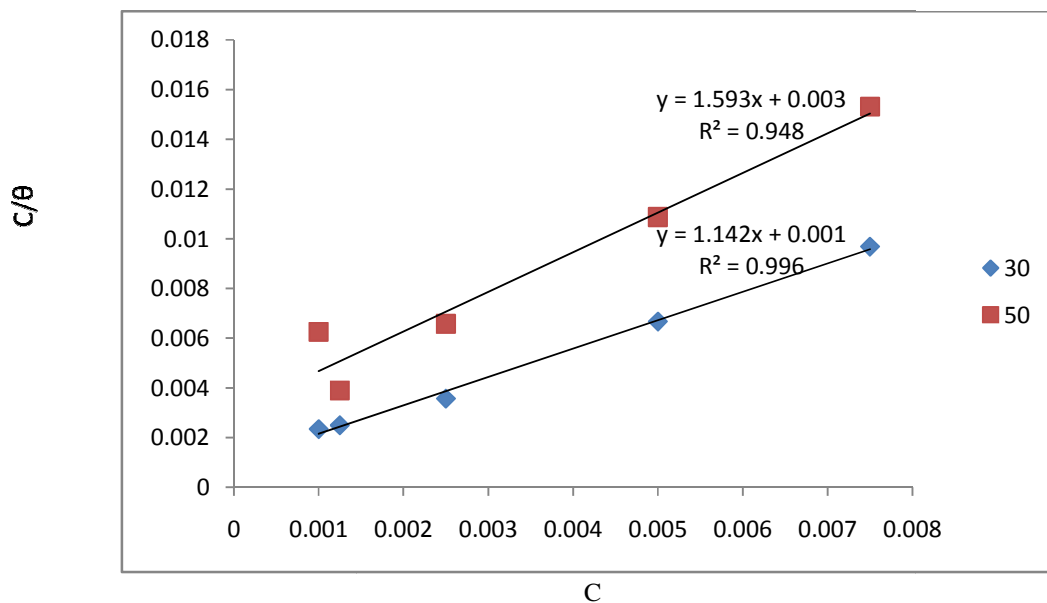


Figure 1.

The slope deviates from unity indicating that there is attraction or repulsion in the adsorbed layer of inhibitor on the aluminium surface. [15, 16].

The standard free energy of adsorption (ΔG°_{ads}) is related to equilibrium constant of adsorption (K_{ads}) according to the following equation [17]

$$K_{ads} = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G^\circ_{ads}}{RT}\right) \tag{3}$$

Where $C_{solvent} = C_{H_2O} = 55.55 \text{ mol dm}^{-3}$, R ($\text{J mol}^{-1} \text{ K}^{-1}$) is the gas constant and T (K) is the temperature.

Table 2 The standard Gibbs free energy of adsorption of HPHPP on the aluminium surface in 1.0 M NaOH

[inhibitor], 10^{-3} M	30°C		50°C	
	θ	$\Delta G^\circ_{ads}, \text{kJ mol}^{-1}$	θ	$\Delta G^\circ_{ads}, \text{kJ mol}^{-1}$
1.00	0.425	-26.762	0.160	-24.288
1.25	0.500	-26.961	0.320	-26.280
2.50	0.700	-27.349	0.380	-25.565
5.00	0.750	-26.236	0.460	-24.587
7.50	0.775	-25.564	0.490	-23.822

The negative values of (ΔG°_{ads}) suggest that the adsorption of inhibitor molecules on to aluminium surface is a spontaneous process [18]. It is seen that the maximum inhibition efficiency was found to slightly decrease from 77.5% to 49.0% with the increase of temperature from 30 to 50°C and it is indicative of physical adsorption of the HPHPP on the aluminium in 1.0 M NaOH [19]. In addition the values of ΔG°_{ads} around -20 kJ mol^{-1} are consistent with physisorption. However the value around -40 kJ mol^{-1} or higher correspond to chemisorptions [20, 21].

Effect of temperature

Thus in examining the effect of temperature on the corrosion process, the apparent activation energies (E_a) was calculated using equation [22]:

$$\text{Log } \frac{r_2}{r_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{4}$$

Where r_2 and r_1 are the corrosion rates at temperatures T_1 and T_2 , respectively. An estimate of heat of adsorption, Q_{ads} , was obtained from the trend of surface coverage with temperature as follows [23]:

$$Q_{ads} = 2.303R \left[\log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right] \times \left[\frac{T_1 T_2}{T_2 - T_1} \right] \text{ kJ mol}^{-1} \tag{5}$$

where θ_1 and θ_2 are the degrees of surface coverage at temperature T_1 and T_2 respectively. The calculated values for E_a and Q_{ads} are given (Table 3).

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

[inhibitor] X 10^{-3} , M	E_a , kJ mol^{-1}	Q_{ads} , kJ mol^{-1}
Blank	47.412	--
1.00	63.044	-55.265
1.25	59.928	-30.635
2.50	76.813	-14.558
5.00	78.727	-51.218
7.50	80.595	-51.930

Increased activation energy, E_a in inhibited solutions compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface while either unchanged or lower (E_a) in the presence of inhibitor suggest chemisorptions [24]. It is seen (Table 3) that E_a values were increased with increasing the concentrations of the inhibitor. Showing that the inhibitor retards corrosion at ordinary temperature and its corrosion retarding efficiency is considerably diminished at higher temperatures [25]. The low and negative Q_{ads} values are indicative of less surface coverage with rise in temperature, supporting the earlier proposed mechanism of physisorption [26].

Gasometric technique

The hydrogen evolution (volumetric measurements) for the aluminium in 1 M NaOH containing two different concentrations of the HPHPP at (30°C) as a function of time is presented (fig. 2)

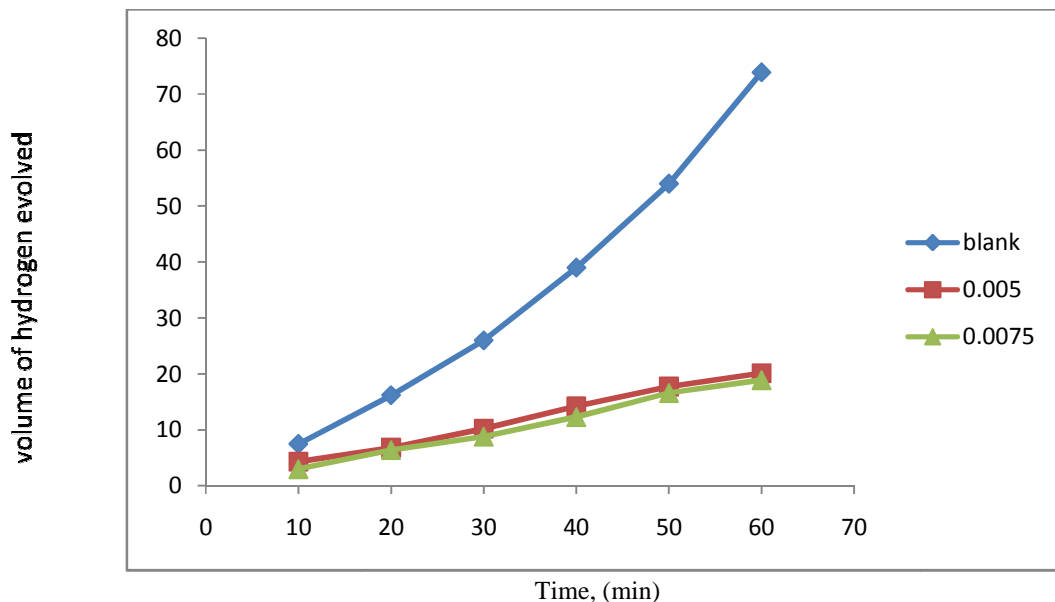


Figure 2.

It is obvious that the introduction of the HPHPP resulted in the reduction of the rate of H_2 evolution as compared to the blank. The inhibition efficiency, I%, is calculated as follows [22].

$$I\% = \left[1 - \frac{V'_{Ht}}{V^{\circ}_{Ht}} \right] \times 100$$

Where V'_{Ht} , the volume of hydrogen is evolved at time t for inhibited solution and V°_{Ht} is the volume of hydrogen evolved at time t for uninhibited solution. The increase in concentrations of HPHPP from 5×10^{-3} to 7.5×10^{-3} , decreased the volume of hydrogen gas evolved and increased the inhibition efficiency summarized in Table.4 Several authors have reported agreement between %I determined from gasometric technique and other techniques of corrosion monitoring, like measurements polarization [27] and weight loss [28].

Table 4 Hydrogen evolution and inhibition efficiency

Time.min	Volume of Hydrogen gas evolved, ml			Inhibition efficiency (I %)	
	Blank	[HPHPP],M		[HPHPP],M	
		5×10^{-3}	7.5×10^{-3}	5×10^{-3}	7.5×10^{-3}
10	7.5	4.3	3.0	43	60.00
20	16.2	6.8	6.4	58	60.49
30	26.0	10.2	8.8	60	66.15
40	39.0	14.2	12.3	64	68.46
50	54.0	17.7	16.6	67	69.26
60	73.9	20.1	18.9	73	74.42

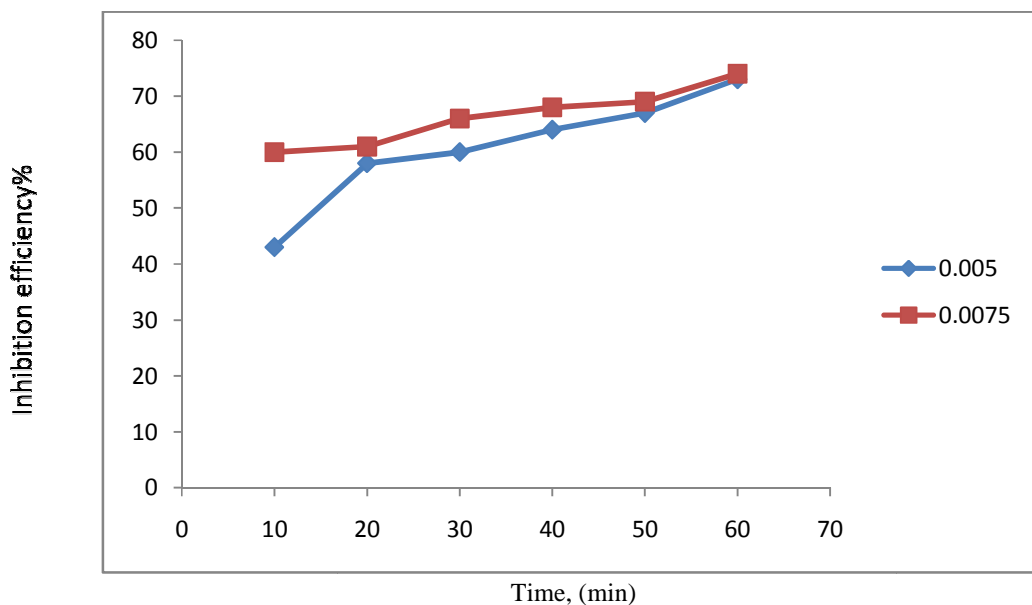


Figure .3

Inhibition efficiency increases with time (Fig.3) and the maximum inhibition efficiency is 74.42% for the inhibitor concentration of 7.5×10^{-3} M and it is in close agreement with the maximum inhibition efficiency values obtained from weight loss method and electrochemical measurements.

Potentiodynamic polarization method

The Tafel Polarization curves of Al in 1.0 M NaOH solution without and with different concentrations of HPHPP are shown (Fig 4) and the polarization parameters such as E_{corr}, I_{corr} ; anodic and cathodic Tafel slopes (β_a, β_c) are summarized in Table 5. Both the anodic and cathodic Tafel slopes were altered significantly, which suggested that the inhibitor exerted an efficient inhibitory effect both on anodic dissolution of metal and on cathodic hydrogen reduction reaction[29]. Literature survey reveals that only when the open circuit potential (OCP) displacement is atleast ± 85 mV in relation to the blank solution , a compound can be recognized as an anodic or cathodic inhibitor [30]. However it is seen (Table 5) that the corrosion potential, E_{corr} , was shifted at the most 40 mV with respect to blank solution and therefore, HPHPP might act as a mixed type inhibitor.

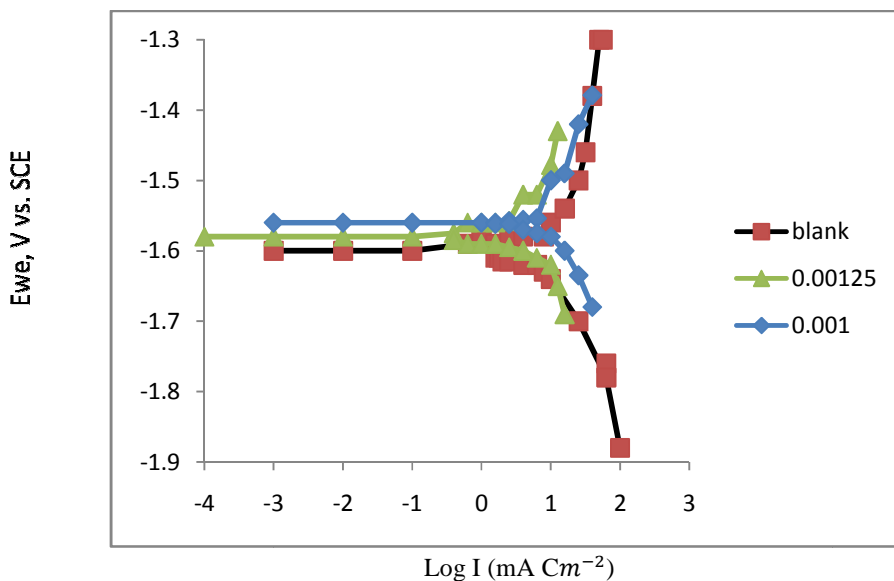


Fig. 4a

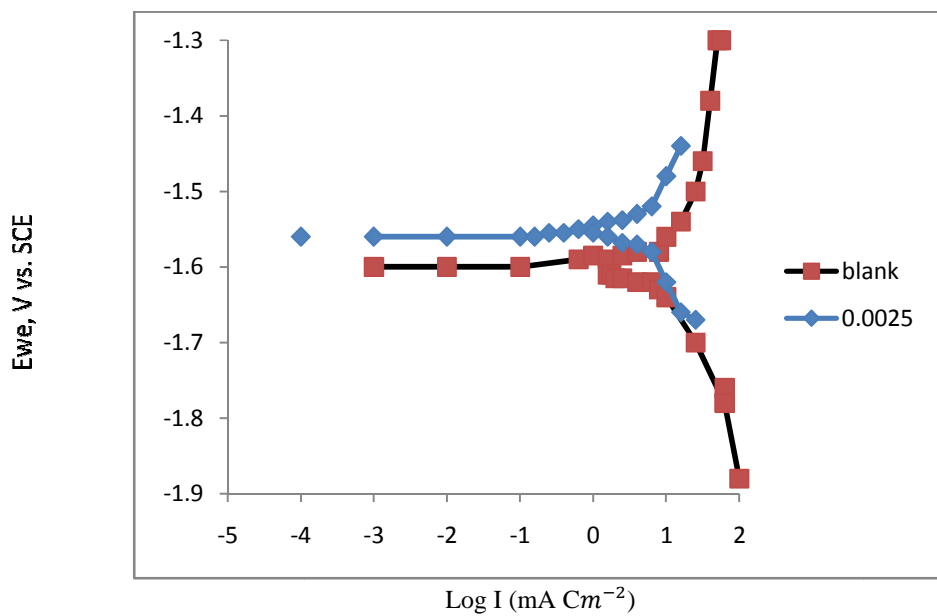


Fig. 4b

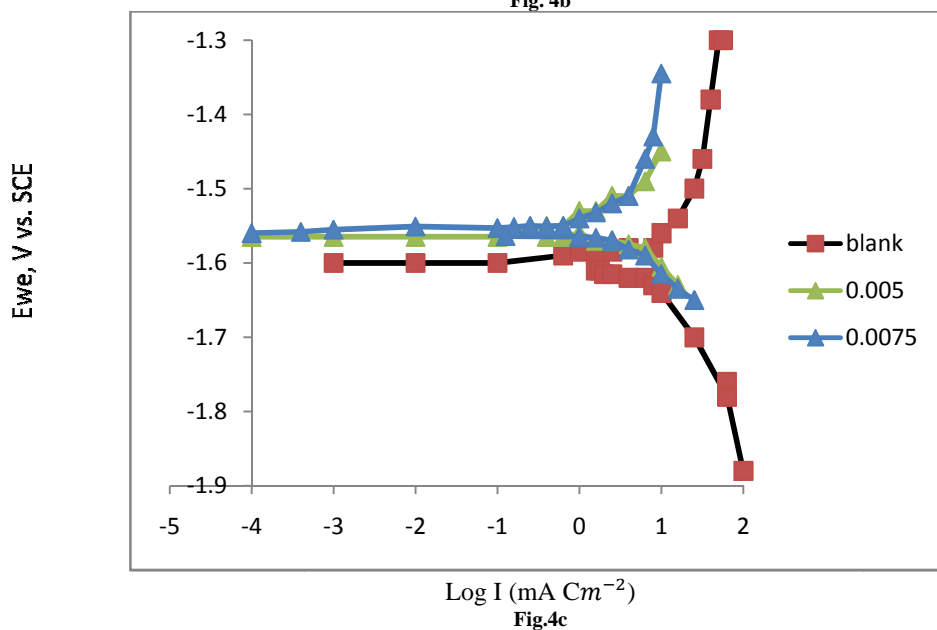


Fig.4c

Table5 Electrochemical polarization parameters for Al in 1M NaOH in the absence and presence of different concentrations of HPHPP.

[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
1.0 x 10 ⁻³	-1.560	10.831	198.4	560.4
1.25 x 10 ⁻³	-1.591	6.144	216.6	410.2
2.50 x 10 ⁻³	-1.554	6.841	196.4	487.6
5.00 x 10 ⁻³	-1.559	5.755	179.2	430.3
7.50 x 10 ⁻³	-1.552	4.911	193.5	475.2

Electrochemical impedance measurements

Nyquist plots of aluminium in 1.0 M NaOH solution in the absence and presence of different concentrations of HPHPP are given (Fig.5.)

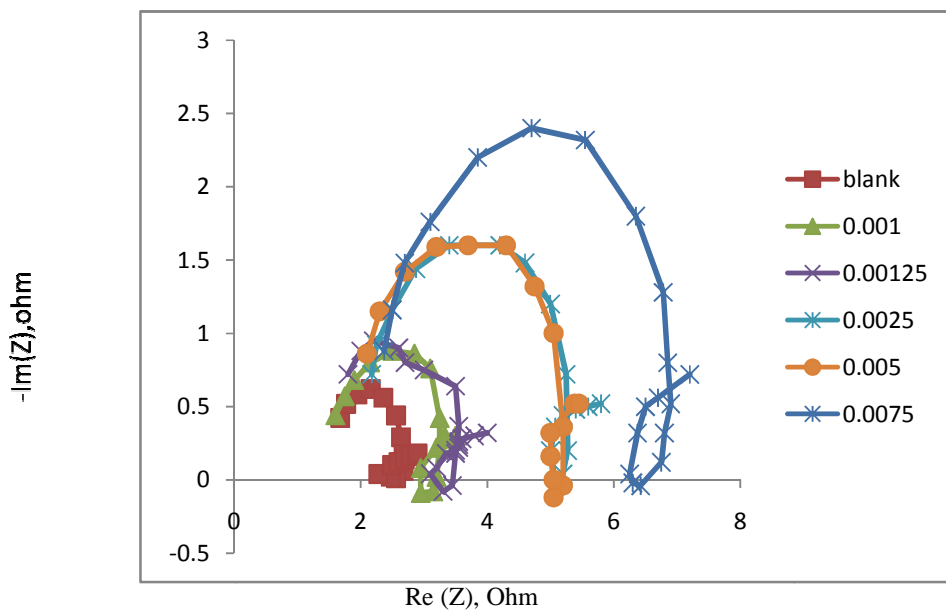


Fig.5

It can be seen from the Nyquist plots that the curves are almost semicircular appearance followed by an inductive loop at the low frequency region. The semicircular nature of the Nyquist plot is due to charge – transfer process, which mainly control the corrosion of aluminium in 1N NaOH solution. Deviation from perfect circular shape is often inferred as the frequency dispersion of interfacial impedance and it may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena. The low frequency inductive loop is probably due to the growth and dissolution of the surface film [31]. The addition of HPHPP to NaOH leads to increase in the size of the capacitive semicircles, and it is indicative of increase in the resistance, R_p , and decrease of double layer capacitance, C_{dl} (Table 6).

Table 6 Impedance parameters for the corrosion of aluminium in 1M NaOH in the absence and presence of different concentration of HPHPP at 30±0.5°C.

Concentrations	R_p , ohm	C_{dl} , μF
Blank	0.9075	55.5
1.0 x 10 ⁻³	1.427	51.78
1.25 x 10 ⁻³	1.723	19.9
2.50 x 10 ⁻³	2.906	54.68
5.00 x 10 ⁻³	3.113	51.04
7.50 x 10 ⁻³	3.899	27.82

CONCLUSION

The inhibition efficiency of HPHPP increases with the increase in inhibitor concentration. The HPHPP control both anodic and cathodic reactions by blocking the active sites of aluminium surface and thus the inhibition are mixed type. The adsorption of HPHPP on aluminium follows the Langmuir adsorption isotherm model. The values of ΔG°_{ads} are suggestive of spontaneous physisorption of the inhibitor. The inhibition efficiency determined by chemical method and electrochemical method are in reasonably good agreement.

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