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Der Chemica Sinica, 2014, 5(3):15-23



Pelagia Research
Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Prevention of aluminium corrosion using [1-(4-hydroxy-3-methoxy phenyl)-3-(3-hydroxy-4-methoxy phenyl) propen-1-one in alkaline medium

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ABSTRACT

Inhibition efficiency of iso-vanillin chalcone in controlling corrosion of aluminium in 1.0N NaOH has been investigated by chemical and electrochemical methods. It was observed that the percentage inhibition efficiency, (%IE) and surface coverage, (θ) increased with increase in the inhibitor concentration and decrease with increase in temperature. It suggests that the inhibitor followed physisorption pathway. The inhibitor was found to obey Langmuir adsorption isotherm at the temperature 303K. The potentiodynamic polarization studies revealed that the inhibitor was mixed type. Surface morphological studies confirmed the adsorption of molecule on the metal surface. Quantum chemical calculations show that the chemisorption process is not possible for studied inhibitor. Simultaneous galvanic and gasometric determinations revealed that as the inhibitor concentration increases, % weight loss for galvanic corrosion increases and % weight loss for gasometric corrosion decreases.

Keywords: Aluminium corrosion, Iso-vanillin chalcone, Mixed type inhibitor, Adsorption isotherm, Galvanic corrosion.

INTRODUCTION

Aluminium can be used as anode material for power sources with high energy densities. Aluminium/air batteries are being currently developed [1], with strong alkaline electrolyte (KOH or NaOH), as power sources for electric vehicle propulsion. However the high reactivity of aluminium in concentrated alkaline solutions results in low coulombic efficiency due to an unacceptably high corrosion rate of the aluminium anode. So, it seemed to be important to discuss the mechanism of corrosion of the aluminium anode and its inhibition in alkaline solutions for the development of aluminium/air batteries. In order to solve the corrosion problem and to maintain the activity of the anode, the study of the effect of addition of organic corrosion inhibitors to the alkaline medium in which Al corrodes, is attempted.

The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface. The lone pair of electrons in hetero atoms determines the adsorption on these molecules on the metal surface [2-9].

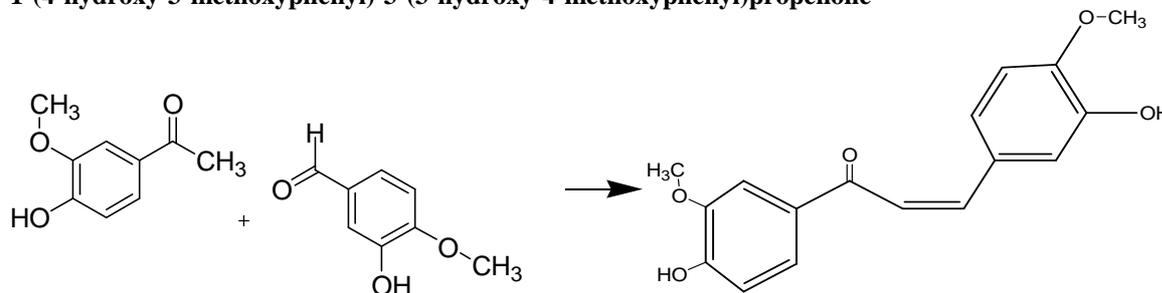
MATERIALS AND METHODS

Sample preparation

For weight loss studies the aluminium strips were cut into coupons of dimension, 2.0 cm x 1.0 cm x 0.14cm from commercially pure aluminium sheet. Each coupon was washed with ethanol, rinsed with acetone and allowed to dry in the air. The aluminium specimens were cut into coupons of dimensions, 8.0 cm x 1.0 cm x 0.14 cm and coated with epoxy resin (araldite) leaving a surface area of 1cm² were used for polarization and impedance studies.

Preparation of iso vanillin chalcone

The mixture of hydroxymethoxyacetophenone and iso-vanillin were mixed in a mortar to this mixture twice the amount of NaOH was added and continue the mixing process. After few seconds of grinding the mixture turned in to a solution and thereafter grinding was continued until the mixture solidified. The product was separated and the separated product washed with cold water filtered with the help of buckner funnel and recrystallized.

1-(4-hydroxy-3-methoxyphenyl)-3-(3-hydroxy-4-methoxyphenyl)propenone

Hydroxymethoxy Isovanillin 1-(4-hydroxy-3-methoxyphenyl)-3-(3-hydroxy-4-methoxyphenyl)-propenone [HMPHMPP]

Weight loss method

Aluminium coupons in triplicate were immersed in 100ml of the 0.1N NaOH containing various concentration of inhibitor. The weight of aluminium coupon before and after immersion was determined using a digital balance [10]. From the initial and final weight of aluminium coupon weight loss and the corrosion rate were calculated. From the weight loss the surface coverage and the inhibitor efficiency were calculated using the equation [11].

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

$$\text{Inhibition efficiency, \% IE} = \frac{w_0 - w_i}{w_0} \times 100$$

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

Electrochemical studies

The electrochemical experiments were carried out using Prinstone 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. In each measurement a fresh working electrode was used. The potentials were scanned, after a stable value of the corrosion potential (E_{corr}) was reached, at a scan rate of 1 mV s⁻¹ from the corrosion potential in the cathodic direction and subsequently in the anodic direction in the potential range of -1800 mV to -1100 mV vs. nOCP. Each experiment was repeated at least three times to obtain reproducible data. The formula used for calculating %IE by electrochemical polarization method was:

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

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

EIS were obtained in the frequency range of 100 kHz–1 Hz and with a.c. signal of amplitude 20 mV. The measurements were taken after the electrode reached a steady value of E_{corr} . The experiments were conducted at a constant temperature of 30°C.

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

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

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

Simultaneous galvanic and gasometric determinations

In a closed vessel containing test solution (1.0 N NaOH without or with inhibitor) weighed Al (anode) is immersed with steel (cathode), Resulting primary cell is connected to an ammeter & a potentiometer in parallel combination. The primary cell is:



When galvanic corrosion of Al occurs, current & voltage are measured, along with volume of H₂ (by a gasometric assembly joined to the vessel) as a function of time. Al was retrieved from the closed vessel and the observed weight loss was determined. From the measured current, weight loss for galvanic corrosion is calculated. From the measured volume of H₂, weight loss for gasometric corrosion is calculated.

Observed weight loss = weight loss for galvanic corrosion + weight loss for gasometric corrosion + weight loss for local cell corrosion

RESULTS AND DISCUSSION

FT-IR spectra of the 1-(4-hydroxy-3-methoxyphenyl)-3-(3-hydroxy-4-methoxy phenyl)-propen-1-one in the presence of (HMPHMPP) was recorded as KBr discs. The absence of a strong band at 1680-1700 cm⁻¹, a strong band at 1720-1740 cm⁻¹ and a strong band at 1665-1685 cm⁻¹ (characteristic of α,β -unsaturated ketones) indicate the conversion of the aldehyde and ketone into the respective chalcone [12]. The presence of strong, broad band at 3200-3400 cm⁻¹ is due to H-bonded O-H stretching.

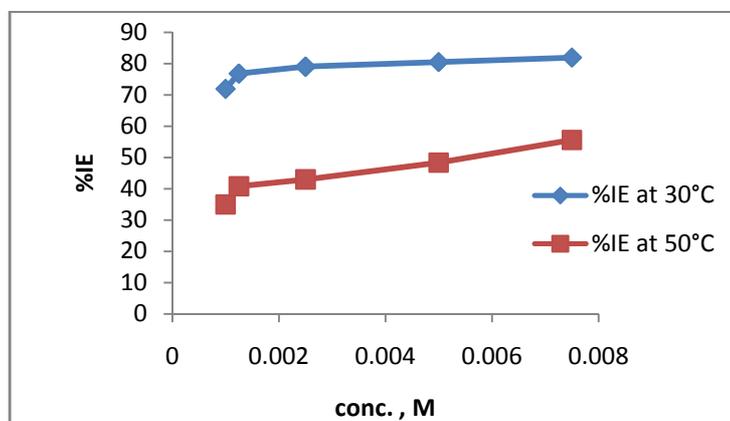
The electronic spectra of the synthesized chalcones were recorded with a UV-visible spectrophotometer (Lambda-35) in the range (200-800 nm) using quartz cell of 1.0 cm length with concentration of samples (10⁻³ M) in ethyl alcohol. A more intense $\pi \rightarrow \pi^*$ band at 200 – 220 nm and a less intense $n \rightarrow \pi^*$ band at 280- 300 nm are obtained for the α, β -unsaturated keto group [13].

The m/z values of molecular ion peak, $M+1$ or $M+Na$ agrees with the formula weight [14-16].

Weight loss method

The surface coverage and %IE of iso-vanillinechalcone have been evaluated in 1.0N NaOH. Table(1) illustrates the effect of concentration of chalcone on the %IE at 30°C and 50°C. It is observed that 7.5x10⁻³ M of chalcone has maximum IE 81.9%. This result denotes that aluminium corrodes in 1.0N NaOH solution but the presence of inhibitor decreased the extent of the aluminium corrosion [17, 18]. The reduction in weight loss of aluminium samples as inhibitor concentration increases may be attributed to adsorption of inhibitor on surface of aluminium and form a barrier film over the aluminium surface. Thereafter the inhibitors impede corrosion process either by merely blocking reaction sites or by altering mechanism of anodic and cathodic processes [19]. The %IE values were plotted against the concentration values of the chalcone at a temperature 30°C and 50°C. From the plot the chalcone showed higher %IE in 30°C than in 50°C it attribute to increase in the solubility of the protective films at the higher temperature [20].

Fig.1: %IE Vs [HMPHMPP] plot at the temperature 30°C and 50°C



The inhibition efficiency of the inhibitor increases with increase in concentration of inhibitor HMPHMPP and this behavior indicates that the molecules formed a barrier film on the aluminium surface and %IE decreases with

increase in temperature it attribute to increase in the solubility of the protective flims and of any reaction products precipitated on the surface of the metal.

Table 1: Inhibition efficiency of corrosion of Al in 1.0 N NaOH by the HMPHMPP at 30°C and 50°C by weight loss method

[HMPHMPP], M	%IE at 30°C	%IE at 50°C
1×10^{-3}	71.9	35.0
1.25×10^{-3}	76.8	40.8
2.5×10^{-3}	79.0	43.0
5×10^{-3}	80.5	48.4
7.5×10^{-3}	81.9	55.6

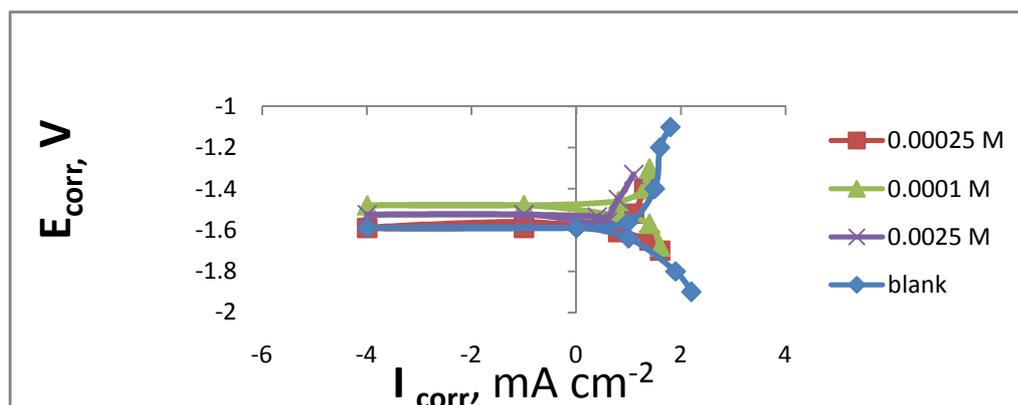
Electrochemical studies

The polarizations results clearly indicate the active corrosion reactions and can thus be correlated with the results obtain in the weight loss methods [21]. The corrosion current densities, I_{corr} , and the corrosion potential, E_{corr} , were determined from the polarization curves by extrapolation of the linear logarithmic segments of the anodic and cathodic Tafel lines to the point of interaction. Electrochemical parameters, such as E_{corr} , I_{corr} , and anodic and cathodic Tafel slopes (β_a , β_c) are listed (Table 2).

Table 2: Potentiodynamic polarization of Al in 1.0 N NaOH without and with varying concentrations of HMPHMPP at 303 K

[HMPHMPP], M	$-E_{\text{corr}}$, V	I_{corr} , mA cm ⁻²	β_c , mV dec ⁻¹	β_a , mV dec ⁻¹	%IE
Blank	1.592	16135.63	270.5	496.5	
1×10^{-4}	1.577	12261.53	276.4	425.1	24.0
2.5×10^{-4}	1.594	9894.47	186.7	549.6	38.7
2.5×10^{-3}	1.550	3575.233	118.0	404.3	77.8

Fig.2: Tafel plot for the inhibitor of [HMPHMPP]



In literature,[22] it is reported that only when the open circuit potential (OCP) displacement is at least 85 mV in relation to the one measured for the blank solution[23,24] can a compound be recognized as an anodic or cathodic inhibitor. In the present investigation it is found that the displacement, at the most, is 40 mV with respect to the E_{corr} of the blank solution. Therefore the inhibitor used in this study is considered to act as mixed-type inhibitor [25].

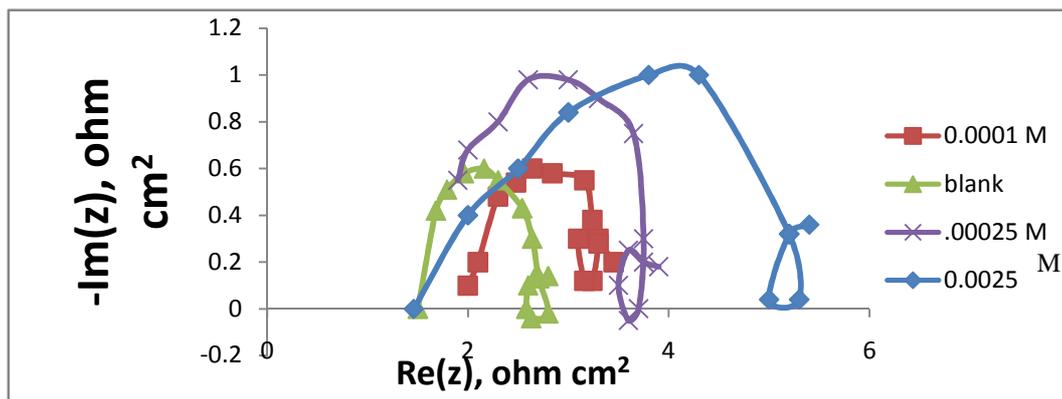
Impedance method

Impedance measurements have been carried out for aluminium in the alkaline solution in the absence and presence of the HMPHMPP the inhibition efficiency with respect to R_{ct} values are given in table. The impedance diagram consists of a large capacitive loop at high frequency. The value of R_{ct} increases and C_{dl} decreases with the increase in concentration of HMPHMPP 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 HMPHMPP on aluminium surface.

Table 3: Impedance parameters for Al in alkaline medium without and with various concentration of HMPHMPP at 303 K

[HMPHMPP], M	R_{ct} , ohm cm ²	C_{dl} , $\mu\text{F cm}^{-2}$	%IE
Blank	0.9075	55.5	
1×10^{-4}	1.208	41.7	24.9
2.5×10^{-4}	1.668	44.3	45.6
2.5×10^{-3}	1.791	19.1	49.3

Fig.3: Nyquist plot for HMPHMPP



Langmuir adsorption isotherm

An adsorption isotherm is a direct relationship between inhibition efficiency and degree of surface coverage (Θ), at constant temperature for the different concentrations of the inhibitor. The adsorption isotherms provide important clues to the nature of the metal-inhibitor interaction. The weight loss data were fitted to Langmuir isotherm equation which can be expressed as

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

The K_{ads} is the equilibrium constant of adsorption process and it is related to the standard Gibbs free energy of adsorption, ΔG^0_{ads} , by the equation,

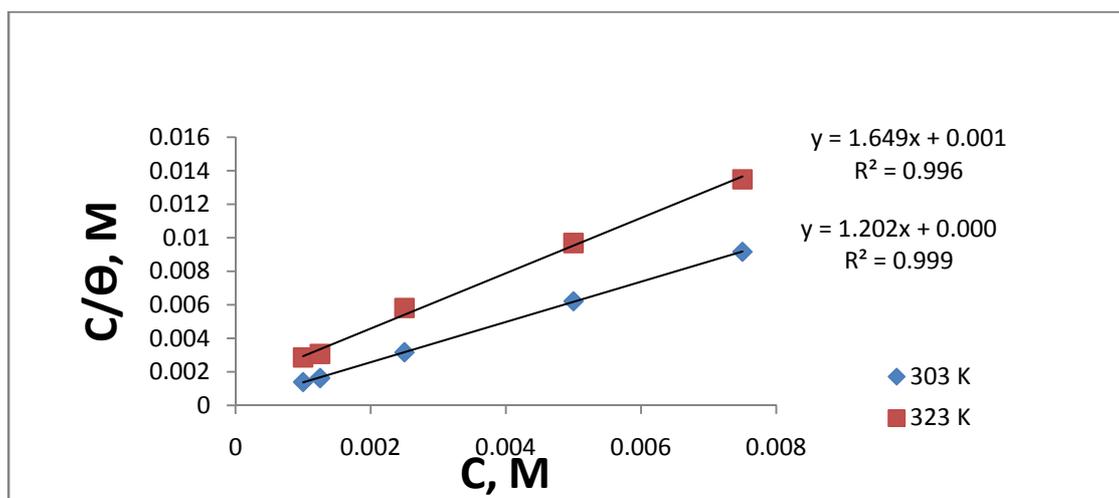
$$K_{ads} = \frac{1}{C_{solvent}} \exp(\Delta G^0_{ads}/RT)$$

The correlation coefficient (R^2) was used to determine the best fit isotherm and it was found that the Langmuir isotherm is the best fit isotherm [26-28] for the systems studied. The value of R^2 indicate strong adherence of the corrosion inhibition process to Langmuir adsorption isotherm [31].

Table 4: Adsorption isotherm readings

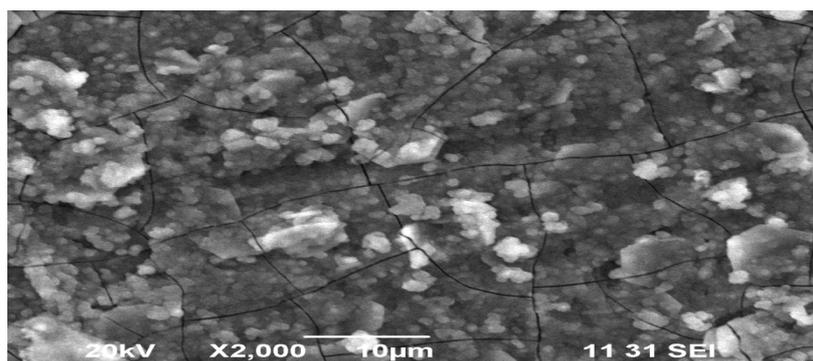
Inhibitor	R^2		Slope		$K_{ads} M^{-1}$		$-\Delta G^0_{ads} kJ mol^{-1}$	
	303K	323K	303K	323K	303K	323K	303K	323K
HMPHMPP	0.9999	0.9964	1.202	1.6494	5000	769.83	31.57	28.64

Fig.4: Langmuir adsorption isotherm for HMPHMPP

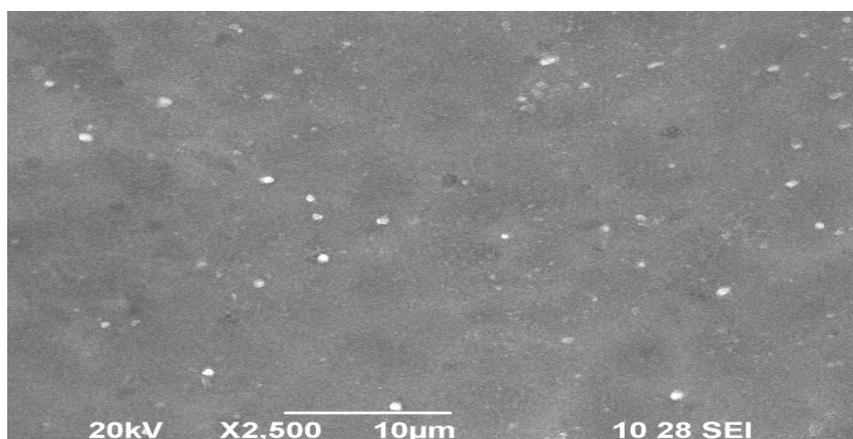


Scanning electron microscopic analysis (SEM)

The surface morphology of Al in solutions of 1.0 N NaOH was studied using SEM.

Fig.5: SEM photograph of aluminium after immersion in 1.0 N NaOH

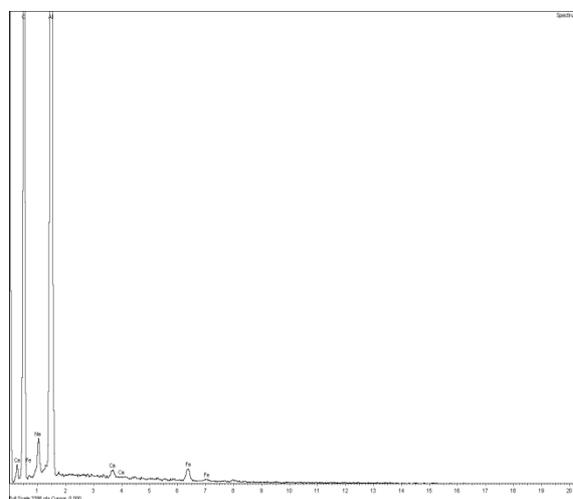
The above SEM image show greater degree of surface deterioration of Al samples immersed in 1.0 N NaOH without inhibitor than for aluminium samples immersed in 1.0 N NaOH with inhibitor.

Fig.6: SEM photograph of aluminium in 1.0 N NaOH with inhibitor HMPHMP

When inhibitor is added to the test solution flakes on the surface of the specimen are reduced when compared with the micrograph of aluminium surface without the inhibitor. In the presence of inhibitor it can be seen that the damaging effect is greatly reduced and the surface is relatively smooth probably due to the formation of protective coverage by the inhibitor [29, 30, 32].

EDX spectra analysis

EDX spectra and elemental composition of aluminium surface after immersion in NaOH solution.

Fig.7: Edx spectra of HMPHMP

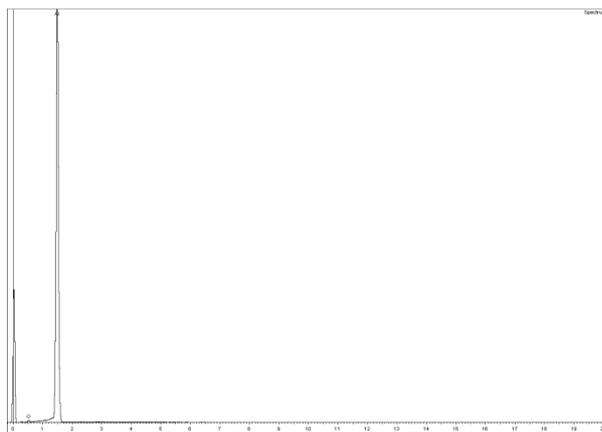
It shows the presence of aluminium, oxygen in 1:2 ratio.

Table 5: Elemental composition Al in blank solution

Element	Atomic Percentage (%)
O	68.80
Al	29.12
Na	1.40

Table 6: Elemental composition of Al Surface immersed in 1.0 N NaOH with HMPHMPP

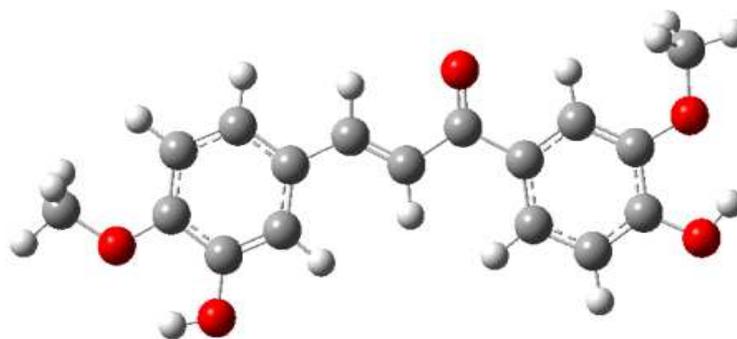
Element	Atomic Percentage (%)
O	5.59
Al	94.41

Fig.8: EDX spectra of aluminium surface immersed in 1.0N NaOH with HMPHMPP

It shows that the concentrations of Al atoms are found higher while the concentrations of oxygen atom are found lower than that of the blank aluminium sample. This result reveals that these inhibitors act as good barriers against the penetration of the aggressive ions in the solution (OH^-) to the aluminium samples.

Quantum Chemical Studies

In order to explore the theoretical experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using standard Gaussian-03 software package. Geometry optimization was carried out by B3LYP functional at the 6-31G (d, p) basis set and at the density functional theory (DFT) level.

**Table 7: Geometry optimization of HMPHMPP**

Inhibitor	%IE	E_{HOMO}	E_{LUMO}	ΔE	ΔN	μ (D)
HMPHMPP	81.9	-5.5679	-1.7508	3.8172	-0.219	3.3416

The number of electrons transferred (ΔN) indicates the tendency of an inhibitor molecule to donate electron to metal atom. The higher the value of ΔN , is the greater the tendency of a molecule to donate electrons to the metal atom. The negative value of ΔN implies that the interaction between the inhibitor and the metal surface does not involve electron transfer. Therefore there is no possibility for chemisorption mechanism [33].

Table 8: Simultaneous galvanic and gasometric determinations

Inhibitor	[inhibitor] $\times 10^{-3}$ M	Measures weight loss, mg	galvanic corrosion		H ₂ evolution	
			Weight loss	% weight loss	Weight loss	% Wt. loss
HMPHMPP	2.50	16.5	5.51	66.6	10.93	33.7
	0.10	44.9	4.68	89.56	40.18	10.51

Simultaneous gassometric and galvanic measurement were given in the above table. It was found that the % weight loss for galvanic corrosion (loss of Al weight in producing current) increased and the % weight loss for gassing corrosion (loss of Al weight in the formation of H₂) decreased proportionate to the concentration of the inhibitor.

CONCLUSION

The maximum inhibition efficiency achieved in the study is 81.9% and it is also found that % IE decreases with increase of testing temperature and it is suggestive of physical adsorption mechanism. The corrosion current densities (I_{corr}), decreases with the increase of inhibitor concentration pointing to the inhibitor adsorption on the metal surface. The E_{corr} values determined, in the presence of various concentrations of the inhibitor, does not show considerable shift indicating physical blocking of the metal surface by the inhibitors. SEM images confirm the formation of the protective coverage by the inhibitor adsorbed on the metal surface. The inhibitor considerably improves the performance of the alkaline primary cell with aluminium anode and steel cathode.

Acknowledgement

My sincere thanks to Dr. T. Jeyaraj, Asst. Prof., PG & Research Dept. of chemistry, JMC, Trichy for his valuable guidance during my project work.

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