Corrosion Inhibition behavior of 3-Hydroxy flavone on Aluminium metal in the Presence of Halide ions in NaOH medium

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ABSTRACT

The anticorrosive effect 3-Hydroxyflavone (3HF) in combination with the halide ions Br^- and I^- for aluminium corrosion in NaOH was studied at the temperature range of 303K-323K using weight loss, potentiodynamic polarization studies and impedance spectroscopic measurements. The inhibition efficiency increased with increase in the concentration of the inhibitor alone and in synergism to a considerable extent on the addition of the halide ions n-Tetrabutylammonium bromide (TBAB) and n-Tetrabutylammoniumiodide (TBAI). The increase in inhibition efficiency and the surface coverage(θ)in the presence of halides were found to be in the order I^- > Br^- which indicates that the radii as well as the electro negativity of the halide ions play an important role in the adsorption process. 3HF obeys Langmuir's adsorption isotherm and the phenomenon of physical adsorption is proposed from the thermodynamics obtained. The mechanism of adsorption is further supported by scanning electron microscopy (SEM).The values of the synergism parameter (S_θ) obtained for the halides are greater than unity suggesting that the enhanced inhibition on the inhibitor caused by the addition of the halide ions is only due to synergistic effect. From the anti-bacterial study it was found that 3HF is more effective for E-coli compared to other organisms.

Keywords:3-Hydroxyflavone, Aluminium, Adsorption isotherm, Anti-microbial studies, Electrochemical impedance spectroscopy (EIS), Krebriella and streptococcus, Proteus, Potentiodynamic polarization, n-Tetrabutylammonium bromide(TBAB), n-tetrabutylammonium iodide (TBAI).

INTRODUCTION

Aluminium is an important subject of research because it is very abundant and easy to handle. In addition it is justified by low price, high electrical capacity and high energy density [1]. In order to mitigate aluminium corrosion, the main strategy is to effectively isolate the metal from the corrosive agents by the use of corrosion inhibitors. Inorganic substances like phosphates, chromates, dichromates and arsenates have been found to be effective corrosion inhibitors but due to their toxicity the alternative corrosion inhibitors, organic substances containing polar functional groups like oxygen, nitrogen and sulphur have reported to exhibit good inhibiting properties [2-6]. Corrosion inhibition occurs via adsorption of the molecules on the corroding metal surface and the efficiency of the inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under a particular condition[7]. As a contribution to the current interest on environmentally friendly, green corrosion inhibitors the present study investigates the inhibiting efficiency of 3HF on aluminium in NaOH. Reports on the effects of halide ions in combination with green inhibitors for corrosion inhibition of metals is very scanty[8-10] therefore the synergistic effect of the additives namely TBAB and TBAI has also been studied.

MATERIALS AND METHODS

Reagents

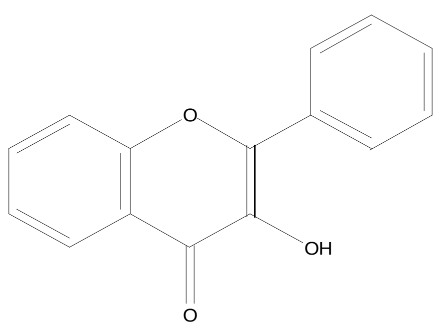
The composition of the commercially pure aluminium used in the present investigation was (wt%) 99.594 Al, 0.002 Cu, 0.003 Zn, 0.100 Pb, 0.050 Co, 0.011 Ni, 0.179 Fe, and 0.082 Cr . The flavonoid compound (*Fig*.1) was purchased from Research Organics Chennai and re-crystallized from methanol.

Recommended procedure

Before each experiment the aluminium specimens was abraded with emery paper of different grades and washed with de-ionized water and degreased with acetone and dried with a stream of air. All chemicals used were of Analytical Grade.

Weight loss studies

Aluminium sheets with dimensions 3.0 x 1.0 x.0.2 cm^3 were used for weight loss studies. The weight loss studies were carried out at 303K, 313K and 323K.



3-HYDROXY FLAVONE

***Fig*.1.**3-Hydroxyflavone (3HF)

The inhibition efficiency was calculated from the corrosion rate [11] using equation 1.

$$\%IE = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \qquad (1)$$

where CR_{blank} and $CR_{inh.}$ are the corrosion rates in the absence and presence of the inhibitor.

Electrochemical measurements

The electrochemical measurements were carried out through a PRINCETON versa STAT Potentiostat - Galvanostat research instrument model by using a conventional three electrode system. aluminium was used as the working electrode with an exposed area of $1cm^2$, saturated calomel as the reference electrode and platinum as the auxiliary electrode. The Electro chemical impedance spectroscopy (EIS) measurements were performed at an open circuit potential after 45 minutes of immersion in the test solution with the amplitude of 10mV. The covered frequency range was 30,000Hz to 1Hz. The impedance diagrams are given as Nquist plots. *Fig*.2 represents the electrical equivalent circuit. The charge transfer values (R_{ct}) were calculated from the difference in the high frequency values. The capacitance of the double layer (C_{dl}) was estimated from the frequency (f) at which the imaginary component of the impedance (Z'') is maximum and obtained from equation 2.

$$f(-Z'') = \frac{1}{2\pi C_{dl} R_{ct}} \qquad (2)$$

The potentiodynamic polarization (PDP) measurements were carried out after the impedance was completed at a sweep range from -1.7V to -1.3V. The Tafel lines extrapolation method was used for finding out the electrochemical parameters like corrosion current density ($I_{corr.}$) and corrosion potential ($E_{corr.}$). The percentage inhibition efficiency can be obtained from the electrochemical measurements using the equations 3 and 4.

$$\text{PDP: } \%IE = \frac{(I_{corr.} - I'_{corr.})}{I_{corr.}} \times 100 \qquad (3)$$

Where $I_{corr.}$ and $I'_{corr.}$ are the corrosion current densities with and without the inhibitor.

$$\text{EIS: \%IE} = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \qquad (4)$$

Where R'_{ct} and R_{ct} are the charge transfer resistances with and without the inhibitor

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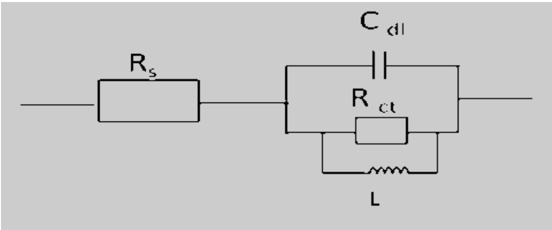

***Fig*.2**. The equivalent circuit model used to fit the ac impedance measurement.

SEM analysis

The specimens for surface morphological examination were immersed in 1 N NaOH with an optimum concentration of the inhibitor and without the inhibitor for 2 hours. Then, they were removed, and rinsed quickly with acetone and dried. The analysis was performed on Hitachi Model S-3000H - Resolution- 3.5 nm.

RESULTS AND DISCUSSIONS

Weight Loss Study

The values of percentage inhibition (%IE) obtained for different concentrations of the inhibitor at different temperatures are given in *Table* 1. From the readings it can be seen that the inhibition efficiency increases as the concentration of the inhibitor increases due to the adsorption of the inhibitor on the metal surface [12]. It is also seen that the inhibition efficiency of the inhibitor decreases with increase in temperature suggesting physisorption [13] and this is attributed to the decrease in the protective nature of the inhibitive film formed on the metal surface or desorption of the inhibitor molecules from the metal surface at higher temperatures [14].The thermodynamic parameters was also calculated and given in *Table* 2.

Table1. Protection performance of 3HF in 1N NaOH at different temperatures

Concentration of inhibitor X10^{-5}M	%IE		
	303K	313K	323K
Blank	-	-	-
1	29.57	27.15	23.81
2	38.51	35.18	34.17
3	47.50	44.10	41.83
4	56.51	50.42	46.33
2+TBAB	68.17	60.05	54.18
2+TBAI	85.98	79.19	71.85

Table2.Thermodynamic parameters of 3HF for aluminium in 1N NaOH

Concentration of inhibitor× 10^{-5}M	E_a kJmol^{-1}	ΔH^o_{ads} kJmol^{-1}	$-\Delta G^o_{ads}$ kJmol^{-1}
Blank	32.82	27.45	-
1	35.53	29.63	36.93
2	36.96	31.11	31.31
3	37.74	31.42	36.10
4	44.46	37.70	36.28
2+TBAB	50.74	-	-
2+TBAI	63.90		

The negative values of ΔG^o_{ads} suggests that the adsorption of the inhibitor on to the aluminium surface is a spontaneous process and the adsorbed layer is stable [15]. The presence of the inhibitor increases the value of the activation energy ($E_{a)}$ as compared to blank indicating physical adsorption of the inhibitor on the metal surface [16-18]. The enthalpy changes (ΔH^o_{ads}) are positive indicating the endothermic nature of the reaction [19].

Potentiodynamic polarization measurements

The anodic and cathodic polarization curves for aluminium in 1N NaOH solution with and without the inhibitor is shown and the anodic and cathodic polarization curves for halide ions is shown in *Fig*.3. and 4. It is clear that both cathode (hydrogen evolution) and anodic (metal dissolution) reactions of aluminium were inhibited with the increasing concentration of the inhibitor. The result suggests that it is a mixed type of inhibitor. The values of the polarization parameters (I_{corr}, E_{corr} and IE%) are listed in *Table3*. The I_{corr} value decreases as the concentration of the inhibitor is increased, hence increasing the inhibitor efficiency.

Table3. Corrosion parameters obtained from PDP measurements for aluminium in 1N NaOH with and without the inhibitor at different concentrations.

Concentration of inhibitor $\times10^{-5}$M	$I_{corr.}$ $mAcm^{-1}$	$-E_{corr.}$ (mv)	IE %
Blank	77.87	1,522.9	-
1	58.71	1,564.9	24
2	55.25	1,555.3	29
3	45.12	1,564.1	41
4	40.93	1,545.4	47
2+TBAB	36.90	1,546.4	52
2+TBAI	15.83	1376.1	79

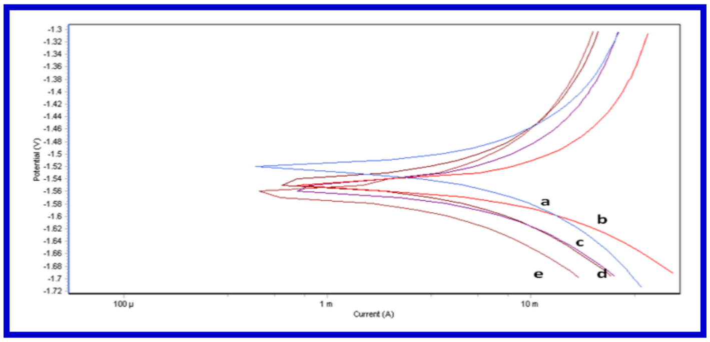

***Fig*.3.** Potentiodynamic polarization curves for Aluminium in 1N NaOH with and without the inhibitor at different concentrations

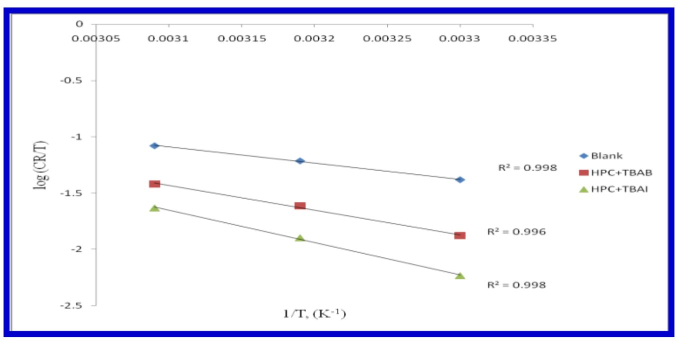

***Fig*.4**.Potentiodynamic polarization curves for Aluminium in 1N NaOH with the halide ions.

Electrochemical Impedance Spectroscopy measurements (EIS)

The EIS of aluminium in 1N NaOH is summarized as Nquist plots in *Fig*.5. The plots clearly show that the addition of increasing amounts of the inhibitor led to an increase in electrochemical impedance [20]. The Nquist plots show three parts: the capacitive loop in the high frequency region, the inductive loop in the middle frequency region and the capacitive loop in low frequency region. The values of R_{ct}, C_{dl} and %IE are evaluated from the Nquist plot (***Fig***.5) and given in *Table*.4. The Complete inspection of the values show that R_{ct} values increases with increasing inhibitor concentration while C_{dl} values decreased with increase in the inhibitor concentration. This was a result of increasing surface coverage which led to an increase in IE%

Table4.Corrosion parameters obtained from EIS measurements for Aluminium in 1N NaOH with and without the inhibitor at different concentrations.

Concentration of inhibitor $\times10^{-5}$M	R_{ct} Ωcm^2	C_{dl} $\mu F/cm^2$	%IE
Blank	0.774	210.49	-
1	1.223	1332.9	24
2	1.397	1192.7	29
3	1.447	1099.1	41
4	2.220	820.4	47
2+TBAB	3.336	90.90	52

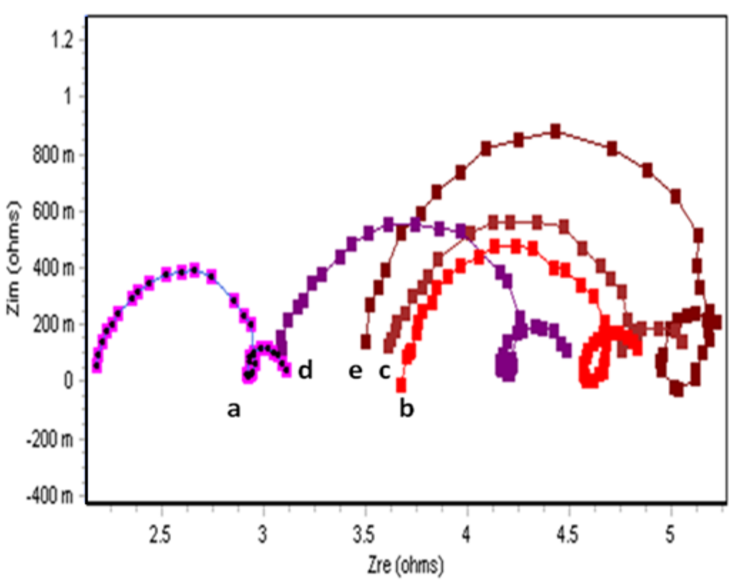

Fig.5. Nquist plots of Aluminium in 1 N NaOH with and without the inhibitor at different concentrations.

Adsorption behavior

To ascertain the nature of the adsorption the surface coverage values for the inhibitor were fitted into different adsorption models like Fruendlich, Tempkin, Langmuir and Frumpkin and the correleation coefficients (R^2) were used to determine best fit which was obtained with the Langmuir adsorption isotherm (*Fig*.6.)

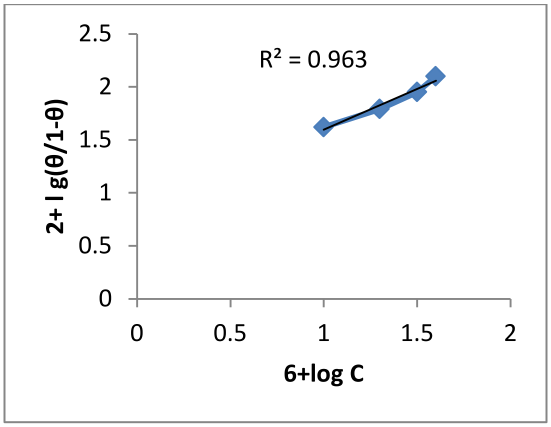

Fig.6. Langmuir adsorption isotherm for 3HF

Synergistic Effect

The inhibition efficiency of the inhibitor was found to be enhanced with the addition of equal volumes of n-tetrabutylammoniumbromide and n-tetrabutylammoniumiodide. Similar observations has been reported by some authors [21] and the enhancement of the inhibition efficiency was ascribed to the synergistic effect. The inhibition efficiency of the inhibitor increases with the addition of the halide ions with the highest inhibition efficiency with iodide ion at all temperatures studied. This can be attributed to the stabilization of adsorbed halide ions by electroststic interaction with the inhibitor which leads to greater surface coverage and inhibition efficiency. Aluminium can form compounds with halide ions, thereby inhibiting the corrosion of Aluminium in the presence of the inhibitor. The syngersitic effect increased in the order $Br^-<I^-$ suggesting a possible role by ionic radii in the adsorption process which also increases in the order Br^- (0.114nm)< I^- (0.135nm). Syngerism can be assessed in terms of the syngerism parameter (S_θ) according to the relationship [22].

$$S_\theta = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}}$$

where $\theta_{1+2} = (\theta_1+\theta_2)(\theta_1\theta_2)$;θ_1 =degree surface coverage by the anions;θ_2 =the degree surface coverage by the cations;θ_{1+2} = the measured surface coverage by both anions and cations. This parameter was calculated from the inhibition efficiency values obtained from the weight loss studies.

***Table*5.** Syngeristic effect of TBAB and TBAI on the inhibition efficiency of 3-HF

Inhibitor	% Inhibition Efficiency	Syngerismparameter,S_θ
3HF TBAB 3HF+TBAB	38.51 38.0 68.17	1.19
3HF TBAI 3HF+TBAI	38.51 42.0 85.98	4.5

SEM Analysis

The SEM images of aluminium were recorded after immersion in 1N NaOH with and without the inhibitor for a time period of 2 hours. The images confirm the change in surface morphology,***Fig.7.*** shows pits on the surface of aluminium and ***Fig.8.*** shows the adsorption of the inhibitor on the aluminium surface.

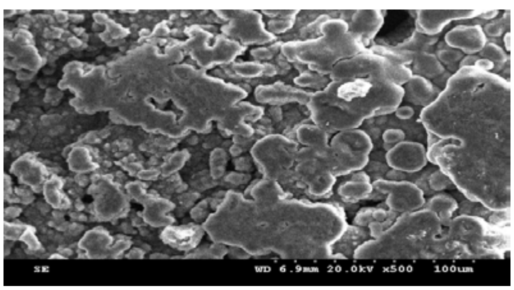

Fig.7. SEM images of Al surface in 1N NaOH for 2 hours at 30^o C.

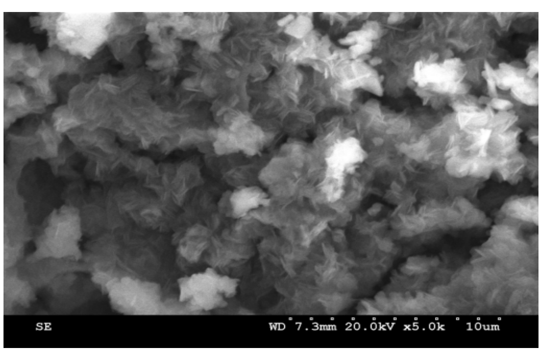

***Fig*.8.** SEM images of Al surface in 1N NaOH with the inhibitor for 2 hours at 30^o C

CONCLUSION

3HF was found to be an effective inhibitor for the corrosion of aluminium in alkaline medium. Electrochemical measurements revealed that 3HF acts as a mixed type of inhibitor. Adsorption of the inhibitor species was found to follow Langmuir adsorption isotherm. The data obtained from weight loss studies, PDP and EIS were found to be in good agreement. The inhibition efficiency of 3HFis temperature dependent and the increase in temperature leads to decrease in the inhibition efficiency of the inhibitor. Synergism studies show that the inhibition efficiency of the flavanoid compound increases with the addition of bromide and iodide ions. The SEM analysis also provided a supporting evidence for the adsorption of the inhibitor on the metal surface.

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