

Corrosion Inhibition of Aluminium using 3-Hydroxy flavone in the Presence of Quarternary Ammonium Salts in NaOH Medium

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(Received November 17, 2011; Accepted February 28, 2012)

ABSTRACT. The anticorrosive effect of 3-Hydroxyflavone (3HF) in combination with quarternary ammonium bromide and iodide salts (QAB and QAI) for aluminium corrosion in NaOH medium was studied at the temperature range of 303K-323K using weight loss study, potentiodynamic polarization study and impedance spectroscopic measurements. The results revealed that the inhibition efficiency increases with the inhibitor concentration and it further increases on the addition of quarternary ammonium bromide and iodide salts. The enhanced inhibition efficiency of the inhibitor in the presence of quarternary ammonium salts may be due to synergistic effect. The adsorption process of 3HF on the aluminium surface obeys Langmuir's adsorption isotherm. The mechanism of adsorption is further supported by Scanning Electron Microscopic study (SEM).

Key words: 3-Hydroxyflavone (3HF), Quarternary ammonium salts, Aluminium, Electrochemical measurements, Synergism

INTRODUCTION

Aluminium is an important subject of research because of its abundance and easiness in handling. In addition aluminium is justified by low price, high electrical capacity and high energy density.¹ In order to control 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 they are toxic in nature. Organic compounds having high electron density at the hetero atoms have the corrosion inhibition efficiency due to the functional groups²⁻⁶ present in aromatic and heterocyclic rings along with electron-rich elements like nitrogen, sulfur and oxygen. Corrosion inhibition occurs via adsorption of the compounds on the corroding metal surface and the efficiency of the inhibition depends on the mechanical structural and chemical characteristics⁷ of the adsorbed layers. As a contribution to the current interest on eco-friendly corrosion inhibitors, the present study is focused on the inhibiting efficiency of 3HF on aluminium in NaOH medium. Reports on the effects of quarternary ammonium salts in combination with green inhibitors for corrosion inhibition of metals is very scanty.⁸⁻¹⁰ Therefore the synergistic effect of the additives namely QAB and QAI has also been studied.

EXPERIMENTAL

Reagents

The commercial aluminium specimen with chemical composition (wt.%): Al(99.594%), Cu(0.002%), Zn(0.003%), Pb(0.100%), Co(0.050%), Ni(0.011%), Fe(0.179%) and Cr (0.082%) was used for the study. The flavonoid compound 3HF (*Fig. 1*) was purchased from Research Organics, Chennai, and re-crystallized from methanol. All chemicals used were of Analytical Grade.

Recommended Procedure

The aluminum specimens were abraded with emery paper of different grades before each experiment and washed with de-ionized water and degreased with acetone and dried with a stream of air.

Weight Loss Study

The aluminium coupons with dimension $3.0 \times 1.0 \times 0.2$ cm³ were used for weight loss studies. The coupons were weighed and the surface areas of all specimens were calculated before and after immersing them in 100 ml test solutions of NaOH with different concentrations for a time period of 2 hours. The weight loss studies were carried out at 303 K, 313 K and 323 K.

The inhibition efficiency was calculated from the corrosion rate¹¹ using the following equation.

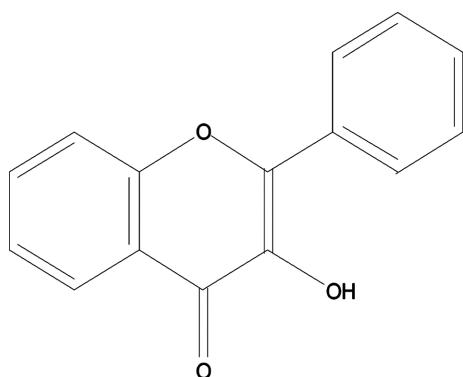


Fig. 1. 3-Hydroxyflavone (3HF).

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

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 using a PRINCETON versa STAT Potentiostat-Galvanostat research instrument and a conventional three electrode cell set up. Aluminium was used as the working electrode with an exposed area of 1 cm^2 , saturated calomel as the reference electrode and platinum as the auxiliary electrode. All electrochemical measurements were carried out for the inhibited and uninhibited solutions. The Electrochemical impedance spectroscopy (EIS) measurements were performed at an open circuit potential after 15 minutes of immersion in the test solution with the amplitude of 10 mV. The covered frequency range was 30,000 Hz to 1 Hz. The impedance diagrams are given as Nyquist plots. Fig. 2 represents the electrical equivalent circuit for the ac impedance measurement. 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 using the following equation

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

The potentiodynamic polarization (PDP) measurements were carried out at a sweep range from -1.7 V to -1.3 V. By the Tafel extrapolation method, 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 following formulae

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

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

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

where R_{ct} and R'_{ct} are the charge transfer resistance values in the absence and presence of the inhibitor respectively.

SEM Analysis

The aluminium specimens were immersed in 1 M NaOH with an optimum concentration of the inhibitor and without the inhibitor for 2 hours. Then, they were removed, rinsed quickly with acetone and dried. The surface morphology was studied using a Hitachi Model S-3000H (Resolution- 3.5 nm) scanning electron microscope.

RESULTS AND DISCUSSION

Weight Loss Study

The values of percentage inhibition efficiency (IE%) obtained for different concentrations of the inhibitor at different temperatures are given in Table 1. From the data

Table 1. Effect of temperature on the inhibition efficiency of 3HF alone and in the presence of quarternary ammonium salts on aluminium in 1 M NaOH by weight loss method

Concentration of inhibitor $\times 10^5\text{M}$	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
3HF+QAB	68.17	60.05	54.18
3HF+QAI	85.98	79.19	71.85

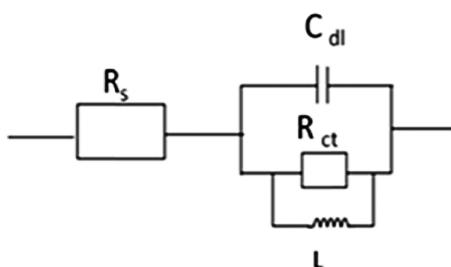


Fig. 2. The equivalent circuit model used to fit the ac impedance measurement.

Table 2. Thermodynamic parameters for the inhibition of corrosion of aluminium in 1M NaOH by 3HF

Concentration of inhibitor $\times 10^{-5}$ M	E_a kJmol $^{-1}$	$-\Delta H_{ads}^o$ kJmol $^{-1}$	$-\Delta G_{ads}^o$ 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

it can be seen that the inhibition efficiency increases as the concentration of the inhibitor increases due to the adsorption of the inhibitor¹² on the metal surface. It is also seen that the inhibition efficiency of the inhibitor decreases with increase in temperature¹³ suggesting physisorption. This may be due to the desorption of the inhibitor molecules¹⁴ from the metal surface at higher temperatures.

The thermodynamic parameters were also calculated (*Table 2*) From the IE (%) values, activation energy (E_a) was calculated using Arrhenius equation. The free energy of adsorption (ΔG_{ads}^o) at different temperatures was calculated using the following equation¹⁵

$$\Delta G_{ads}^o = -RT \ln (55.5 K_{ads})$$

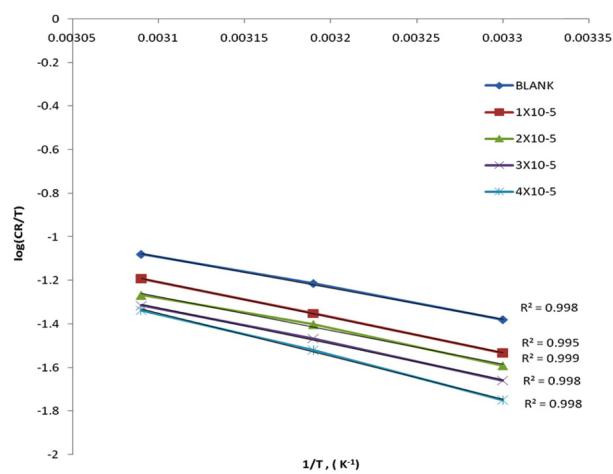
where R is the molar gas constant, T is the absolute temperature and 55.5 is the molar concentration of moles of water in mol/dm 3 . K_{ads} is given by the following expression

$$K_{ads} = \left(\frac{\theta}{1-\theta} \right) \times \frac{1}{C}$$

where θ is the degree of surface coverage (*Table 3*) and C is the concentration of the inhibitor. The enthalpy of activation, ΔH_{ads}^o , is another criterion from which the mode of adsorption can be probed. ΔH_{ads}^o was obtained by applying the transition state equation.

Table 3. Effect of 3HF alone and along with of quaternary ammonium salts on rate of corrosion and surface coverage for aluminium in 1 M NaOH at 303 K

Concentration of inhibitor $\times 10^{-5}$ M	Rate of corrosion g/cm 2 /min	IE (%)	Surface Coverage (θ)
Blank	12.63	-	-
1	8.89	29.57	0.2957
2	7.76	38.51	0.3851
3	6.63	47.50	0.4750
4	5.40	56.51	0.5651
3HF+QAB	4.02	68.17	0.6817
3HF+QAI	1.77	85.98	0.8598

**Fig. 3.** Thermodynamic plot for HPC at 303, 313 and 323 \pm 1 K.

$$CR = \frac{RT}{Nh} \exp\left[\frac{\Delta S_{ads}^o}{R}\right] \exp\left[-\frac{\Delta H_{ads}^o}{RT}\right]$$

where CR is the corrosion rate, h the Planck's constant, N the Avogadro's number, ΔS^o the entropy of activation, T the absolute temperature and R the universal gas constant. A plot of $\log (CR/T)$ against $1/T$ (*Fig. 3*) was made for the blank and different concentrations of the inhibitor. From the slope value, ΔH_{ads}^o values were computed.

The negative values of ΔG_{ads}^o suggest that the adsorption of the inhibitor on to the aluminum surface is a spontaneous process and the adsorbed layer is stable.¹⁶ The presence of the inhibitor increases the value of the activation energy (E_a) indicating physical adsorption¹⁷⁻¹⁹ of the inhibitor on the metal surface. The enthalpy changes (ΔH_{ads}^o) are negative indicating the exothermic²⁰ nature of the adsorption process.

Potentiodynamic Polarization (PDP) Measurements

The anodic and cathodic polarization curves for aluminium in 1 M NaOH solution with and without the inhibitor are shown in *Fig. 4.* and *5*. It is clear that both cathodic (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 *Table 4*. As the inhibitor concentration increases, the I_{corr} value decreases thereby increasing the inhibition efficiency.

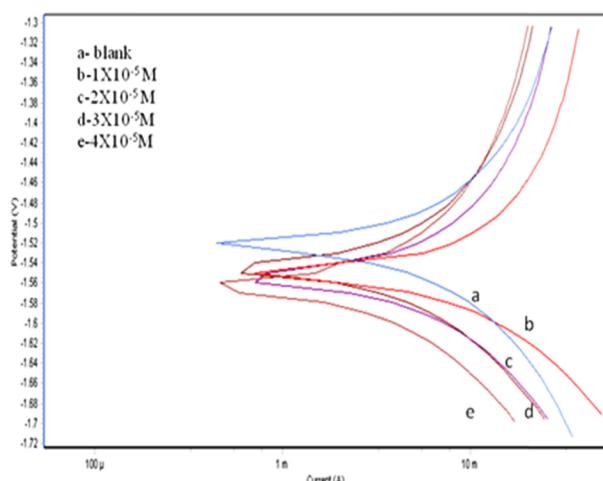


Fig. 4. Potentiodynamic polarization curves for aluminium in 1 M NaOH with and without the inhibitor at different concentrations.

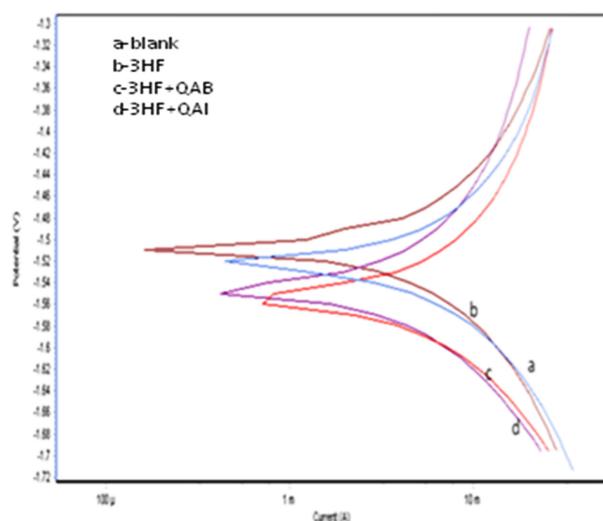


Fig. 5. Potentiodynamic polarization curves for aluminium in 1 M NaOH with the quarternary ammonium salts.

Table 4. Potentiodynamic polarization parameters for aluminium in 1 M NaOH with and without the inhibitor at different concentrations

Concentration of inhibitor $\times 10^{-5}$ M	$I_{corr.}$ $\mu A/cm^2$	$-E_{corr.}$ (mV)	IE(%)
Blank	77,837	1,522.9	-
1	58,714	1,564.9	24
2	55,256	1,555.3	29
3	45,124	1,564.1	41
4	40,933	1,545.4	47
3HF+QAB	36,906	1,546.4	52
3HF+QAI	15,835	1,376.1	79

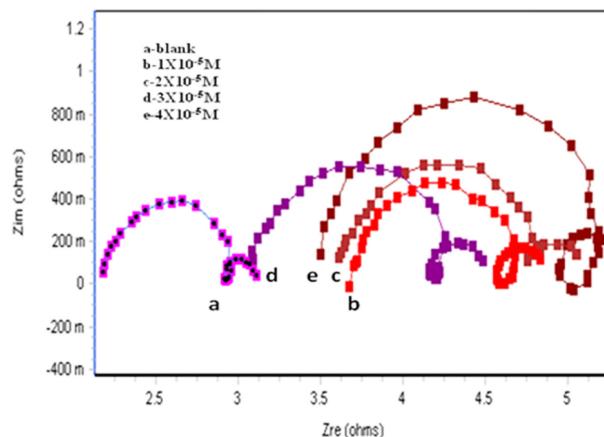


Fig. 6. Nyquist plots of aluminium in 1 M NaOH with and without the inhibitor at different concentrations.

Table 5. Corrosion parameters obtained from EIS measurements for aluminium in 1 M NaOH with and without the inhibitor at different concentrations

Concentration of inhibitor $\times 10^{-5}$ M	R_{ct} Ωcm^2	C_{dl} $\mu F/cm^2$	IE(%)
Blank	0.774	210.49	-
1	1.000	1332.9	22
2	1.121	1192.7	30
3	1.214	1099.1	36
4	1.630	820.4	52
3HF+QAB	1.841	72.48	58
3HF+QAI	2.170	61.60	64

Electrochemical Impedance Spectroscopy (EIS) Measurements

The EIS of aluminium in 1M NaOH is summarized as Nyquist plots in Fig. 6. The plots clearly show that the addition of increasing amounts of the inhibitor causes an increase in electrochemical impedance.²⁰ The Nyquist 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 given in Table 5. The complete inspection of the values shows that R_{ct} values increases while C_{dl} values decreases with increase in the inhibitor concentration. This may be due to the increased surface coverage which led to an increase in IE(%).

Adsorption Behavior

To ascertain the nature of adsorption of 3HF on aluminium in 1 M NaOH attempts were made to fit various isotherms such as Freundlich, Temkin, Langmuir and Frumkin. However the best fit was obtained (Fig. 7) only with Langmuir adsorption which supports the monolayer

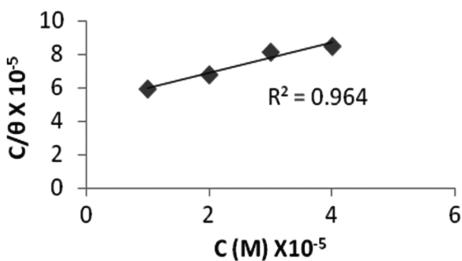


Fig. 7. Langmuir adsorption isotherm for 3HF.

Table 6. Synergistic effect of QAB and QAI on the inhibition efficiency of 3HF (from weight loss studies)

Inhibitor	Inhibition Efficiency (%)	Synergism Parameter, S_θ
3HF	38.51	
QAB	38.0	1.19
3HF+QAB	68.17	
3HF	38.51	
QAI	42.0	4.5
3HF+QAI	85.98	

adsorption of the inhibitor on the aluminium surface.

Synergistic Effect

The inhibition efficiency of the inhibitor was found to be enhanced with the addition of n-tetrabutylammonium bromide and n-tetrabutylammonium iodide along with 3HF. Similar observations has been reported²² earlier 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 quaternary ammonium salts at all temperatures studied. This can be attributed to the stabilization of adsorbed quaternary salts by electrostatic interaction with the inhibitor. This leads to greater surface coverage and higher inhibition efficiency. The synergistic effect of I⁻ is found to be greater than Br⁻ suggesting a possible role by ionic radii in the adsorption process. Synergism can be assessed in terms of the synergism parameter (S_θ) according to the following relationship²³

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

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, θ_1 is the surface coverage by flavonoid compounds, θ_2 the surface coverage of the additive and θ'_{1+2} is the measured surface coverage for flavonoids in combination with additives.

SEM Analysis

The SEM images of aluminum were recorded (Figs. 8

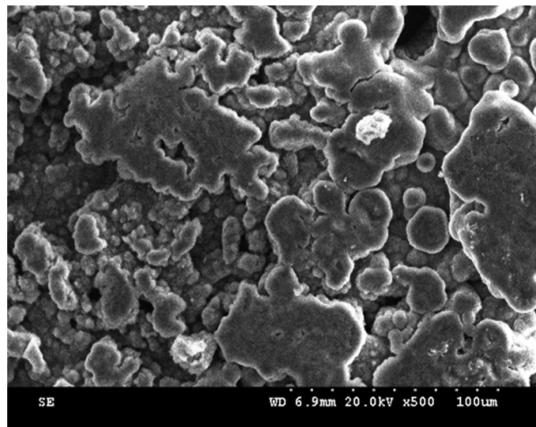


Fig. 8. SEM image of Al specimen kept in 1 M NaOH for 2 hours at 303 K.

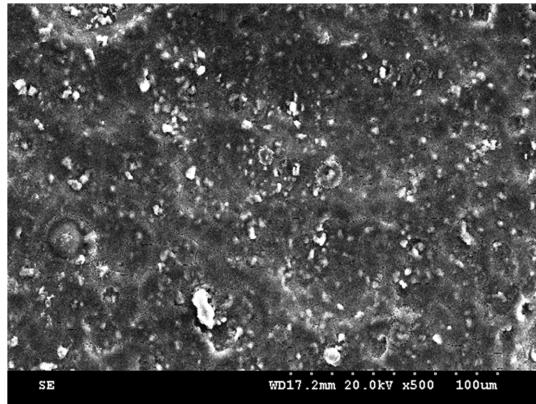


Fig. 9. SEM image of Al specimen kept in 1 M NaOH along with 3HF for 2 hours at 303 K.

and 9) after immersion in 1 M NaOH with and without the inhibitor for a time period of 2 hours to establish the interaction of the organic molecules with the metal surface. The images of SEM confirm the changes in the surface morphology. In the absence of the inhibitor, extensive corrosion is suffered by the metal surface which is evident by the presence of hemispherical deep pits and corrosion products (Fig. 8) which is due to the attack of the alkali on the surface. The specimen immersed in the alkali along with the inhibitor has a less corroded surface. This indicates that the inhibitor molecules hinder the dissolution of aluminium by forming an organic protective film on the metal surface and thereby reducing the rate of corrosion.

CONCLUSION

The flavonoid compound 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. The adsorption of the inhibitor molecules was found to follow Langmuir adsorption isotherm. The data obtained from weight loss studies, potentiodynamic polarization and electrochemical impedance spectroscopic measurements were found to be in good agreement. The inhibition efficiency of 3HF is temperature dependant and the increase in temperature leads to decrease in the inhibition efficiency of the inhibitor. Synergism studies show that the inhibition efficiency of the flavonoid compound increases with the addition of quarternary ammonium bromide and iodide salts. The SEM analysis also provided a supporting evidence for the adsorption of the inhibitor on the metal surface.

Acknowledgement. The authors would like to thank the Principal and Management of Bishop Heber College (Autonomous), Tiruchirapalli -620 017 for the encouragement and the UGC (New Delhi) for financial support.

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