



Spectroscopic Methods Used For Analyzing Protective Film Formed By Al in Sodium Chloride

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ABSTRACT

Corrosion of Aluminum metal at pH 10 has been controlled by di carboxylic Acids of Oxalic acid (OA) and Adipic Acid (AA). The Inhibition Efficiency (IE) has been determined by the Classical Weight Loss Method. The Maximum Inhibition Efficiency (IE) offered by the Oxalic acid (OA) and Adipic Acid (AA) 250ppm and Zn²⁺ 50ppm system is 88 and 96%. To determine the Protective film is found to be UV- Visible absorbance spectra, Fluorescent and Infra Red spectra has been used.

KEYWORDS: Aluminium at pH 10, Oxalic acid and, Adipic Acid, UV- visible, Fluorescent and IR spectra.

1.INTRODUCTION

Aluminium is the second most rich metal after Iron because of its little atomic mass and negative average electrode prospective. Aluminium theater a major responsibility in distinct human being activities. Because of its High energy density, it attracts the Anode material for influence sources. Due to its strong electrical conductivity and good potency, it is used in Construction, Packing and shipping. Aluminium is commonly used by people because it is simply obtainable. It is used in numerous Industries, since it has high energy density, strength and purity.[1]. Though Aluminium has adhesive shielding passivating oxide layer, this layer is amphotericly susceptible. It is establish that Aluminium metal dissolves in acidic solution and in basic solution [2-3]. Though Orsted discovered Aluminium (Latin – alumen, alum), Thanks to Wohler who isolated Aluminium [4]. Aluminium was extracted from Bauxite ore by Pierre Breathier [5]. The Principle technique used in extraction of Aluminium have been separately developed by Charles Martin Hall of Ohio in U.S and Paul Heroult of France which is commonly referred as Hall - Heroult electrolytic procedure. Since of having 59% Copper conductivity, Aluminium behaves as a excellent thermal and electrical conductor. Aluminium is an excellent Super Conductor [6] and it is one of the mainly generally used Non Ferrous metal[7]. It is observed



that global fabrication of Aluminium is very high [8,9]. A high proportion of Aluminium alloys is used for producing Aluminium foils and beverage cans [10].

Aluminium products can be used with very high effectiveness [11]. Metal and alloys decay when they come in contact with environment, especially in presence of oxygen and water. This impulsive, natural and thermodynamically favorable process is known as Corrosion [12-14]. When Aluminum is exposed to air, first it undergoes corrosion and an oxide layer is generated from prevents further Corrosion of the metal [15].

The present work is undertaken

1. To evaluate the inhibition efficiency (IE) of oxalic acid (OA) and adipic acid (AA) is scheming deterioration of aluminium in an sedimentary resolution incorporating 60 ppm of Cl⁻ at pH 10 in the absent and in the present of Zn²⁺ by mass (or) weight loss method.
2. To investigate the protecting layer produced on the metal plane, UV-visible absorption spectroscopy, fluorescence spectroscopy, Fourier-transform infrared spectroscopy (FTIR)

2. EXPERIMENTAL SECTION

2.1. Specimens Preparation

Commercial Aluminium specimens containing 95% pure Aluminium of requisite measurement 4.0 x 1.0 x 0.2 cm. The specimens were elegant to get mirror concluding. After polishing, the specimens were used in this work.

2.2. Inhibitor Solution

In 100 ml of double distilled water and NaOH solution, 1 g of oxalic acid and adipic acid was dissolved. The pH of this Inhibitor solution was adjusted to 10.

2.3. Weight Loss Method

Three Aluminium specimens were immersed in 100 ml of an aqueous solution at pH 10 (dilute sodium hydroxide solution) for one day in the absence and presence of Inhibitors and the synergist namely Zn²⁺. The weight of the specimens were determined using a sensitive balance Shimadzu AY62 model before immersion and after immersion for one day. The Corrosion rates were calculated. The Inhibition Efficiency (IE) was calculated from the equation.

$$\text{Inhibition Efficiency (IE)} = [(w_1 - w_2) / w_1] \times 100\%$$



Where w_1 = Corrosion rates in the presence of the Inhibitor.

w_2 = Corrosion rates in the absence of the Inhibitor.

2.4. UV- Visible Absorbance Spectra

UV –Visible Absorbance Spectra of solutions of metal Inhibitor complexes were recorded in a UV Spectra S-100 Spectrophotometer.

2.5. Fluorescence Spectra

Fluorescence Spectra of metal Inhibitor complexes were recorded in a F-6300 Spectra Fluorimeter.

2.6. FTIR Spectra

FTIR Spectrophotometer of Perkin Elmer -1600 series was used to record the FTIR Spectra of pure Carboxylic Acids and the protective film (KBr method).

3.RESULTS AND DISCUSSIONS

3.1 Analysis of Weight Loss Method

Corrosion Rate (CR) of Aluminium immersed in aqueous solution containing at $\text{pH}=10$ for one day in the absence and presence of Inhibitor oxalic acid(OA) and Adipic Acid (AA) has been evaluated and values are given in the Tables 1 and 2. The Inhibition Efficiencies of OA and AA are also given in these Tables. The Inhibition Efficiencies of the OA Zn^{2+} and AA- Zn^{2+} systems as a function of concentration of OA and AA are shown in. It is observed from Table 1 that OA and AA shows some Inhibition Efficiencies and Inhibition Efficiency (IE) increases when the concentration increases. For example, 50ppm OA has 70 percent and AA has 78 percent IE while 250ppm OA has 76 percent and 250ppm AA has 86 per cent. This is due to the fact that as the concentration of OA and AA increases, the protective film (probably Aluminium OA and AA complex) formed on the metal surface goes on increasing.

Table 1: Corrosion rates (CR) of Aluminium immersed in aqueous solution containing in the absence and presence of Inhibitor system at various concentration and the Inhibition Efficiencies (IE) obtained by Weight Loss Method for the immersion period of one day.



Cl ⁻ ppm	AA Ppm	Zn ²⁺ Ppm	CR Mdd	IE %
60	0	0	23.48	--
60	50	0	5.16	78
60	100	0	4.69	80
60	150	0	4.46	81
60	200	0	3.99	83
0	250	0	3.28	86

Cl ⁻ ppm	OA ppm	Zn ²⁺ ppm	CR mdd	IE%
60	0	0	23.48	--
60	50	0	7.04	70
60	100	0	6.57	72
60	150	0	6.10	74
60	200	0	5.87	75
60	250	0	5.63	76

Role of Zn²⁺ is Increasing the Inhibitive Property of Adipic acid(AA) and Oxalic Acid (OA)

The role of Zn²⁺ is increasing the inhibitive property of adipic acid (AA) and oxalic acid (OA) is given in Table 2. The adipic acid and oxalic acid shows excellent inhibitive property in the extinct of Zn²⁺ (50 ppm). For instance the mixture consisting of adipic acid and oxalic acid (250 ppm) and Zn²⁺ (50 ppm) offers 96% and 88% corrosion inhibition efficiency. This concept is known as synergistic effect. In presence of Zn²⁺, more inhibitor molecules are transported towards the aluminium metal surface. This enhances the formation of metal inhibitor compound on the anodal sites of the metal surface, while, cathodic sites are covered by Zn(OH)₂. Thus anodal response and cathodal response are restricted efficiently. This statements for the synergistic effect and enhanced inhibitive efficiency of the inhibitor - Zn²⁺. The bond between inhibitor molecule and Zn²⁺ is tough adequate to carry the inhibitor molecule to the metal surface and weedy adequate to rupture in occurrence of the metal ion, on the plane of a metal.

Table 2: Corrosion Rates (CR) of aluminium submerged in sedimentary solution incorporated 60 ppm Cl⁻ ions in the absence and presence of inhibitor scheme at different absorption and the Inhibition Efficiency (IE) attained by weight loss method(Inhibitor system: AA and OA +50 ppm of Zn²⁺ Immersion period: 1 day pH = 10)

Cl ⁻ ppm	AA ppm	Zn ²⁺ ppm	CR mdd	IE %
60	0	0	23.48	--
60	0	50	19.25	18
60	50	50	2.58	89
60	100	50	2.11	91
60	150	50	1.87	92
60	200	50	1.40	94
60	250	50	1.17	96



Cl ppm	OA ppm	Zn ²⁺ ppm	CR mdd	IE %
60	0	0	23.48	--
60	0	50	19.25	18
60	50	50	4.46	81
60	100	50	3.75	84
60	150	50	3.52	85
60	200	50	3.05	87
60	250	50	2.87	88

3.2 Analysis of UV-Visible spectra

The UV-visible absorption spectrum of an sedimentary solution containing AA is exposed in Figure 1(a). A peak appears at 418 nm. When Al³⁺ (Al₂(SO₄)₃) is added, a peak appears at 421 nm and there is an increases in intensity. This is exposed in Figure 1 (b) and indicates that a complex in solution is formed between AA-Al³⁺

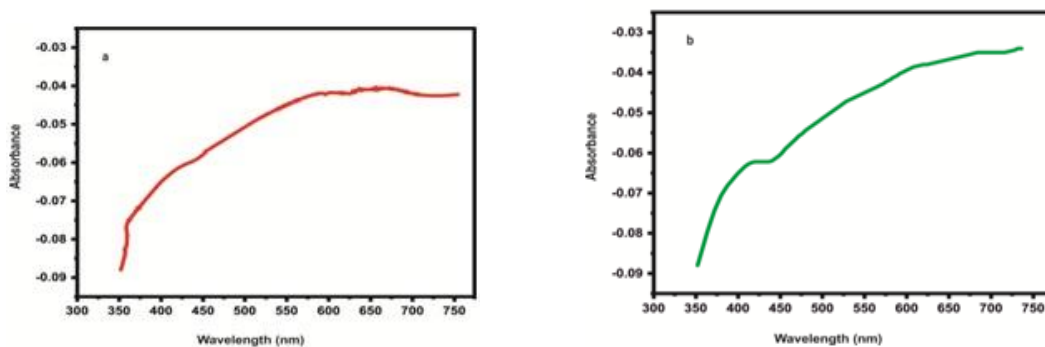


Figure 1 UV visible absorbance or optical activity spectrum of (a) AA and (b) AA + (Al₂(SO₄)₃)

The UV-visible absorption spectrum of an sedimentary solution containing OA is shown in Figure2(a). A peak appears at 338 nm. When Al³⁺ (Al₂(SO₄)₃) is added, a peak appears at 410 nm and there is an increases in intensity. This is shown in Figure2(b) and indicates that a complex in solution is formed between OA-Al³⁺

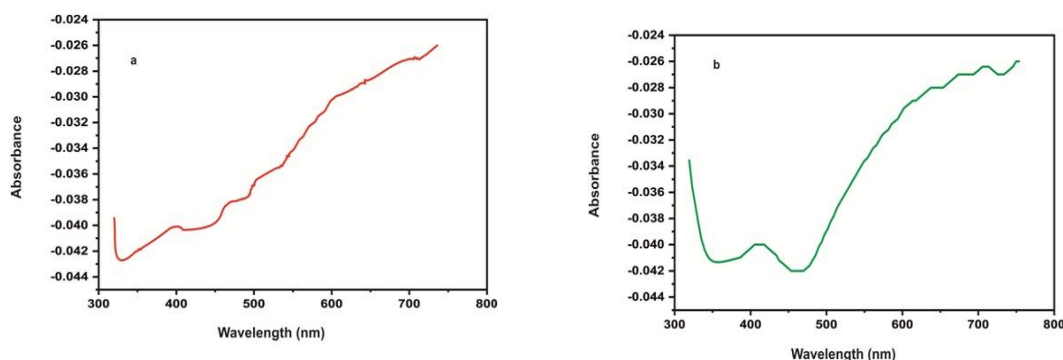


Figure 2 UV visible absorbance spectra (a) OA and (b) OA + $(\text{Al}_2(\text{SO}_4)_3)$

3.3. Analysis of the Fluorescence Spectra

Fluorescence spectrum is to be used to identify the occurrence of metal ion inhibitor compound produced on the metallic plane. It is used to identify the formation of Al^{3+} -AA complex in solution. The emission spectrum ($\lambda_{\text{ex}}=300\text{nm}$) of the AA+ Al^{3+} solution is shown in the Figure 3(a). A peak appears at 425 nm. The emission spectrum ($\lambda_{\text{ex}}=300\text{nm}$) of the layer produced on the metallic plane behind submersion in the resolution including 250 ppm of AA and 50 ppm of Zn^{2+} is exposed in Figure 5.6(b). A peak appears at 427nm. This matches with the peak of Al^{3+} -AA complex. This indicates that there is a complex formed between AA and Zn^{2+} on the metallic surface.

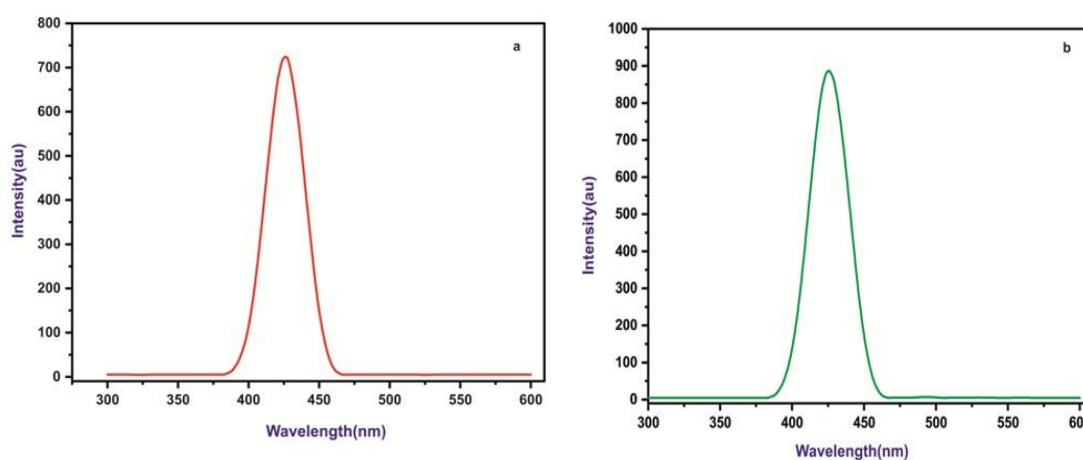




Figure 3 Fluorescence spectrum of (a) AA + Al³⁺ blank (b) protecting layer produced on the surface of aluminium behind submersion in the resolution containing 250 ppm of AA + 50 ppm of Zn²⁺

Fluorescence spectrum is to be used to identify the occurrence of metal ion inhibitor compound produced on the metallic plane. It is used to identify the formation of Al³⁺-OA complex in solution. The emission spectrum ($\lambda_{ex}=300\text{nm}$) of the OA+Al³⁺ solution is shown in the Figure 4(a). A peak appears at 384 nm. The emission spectrum ($\lambda_{ex}=300\text{nm}$) of the layer produced on the metallic plane behind submersion in the resolution including 250 ppm of OA and 50 ppm of Zn²⁺ is shown in Figure 4(b). A peak appears at 427 nm. This matches with the peak of Al³⁺-OA complex. This indicates that there is a complex formed between OA and Zn²⁺ on the metal surface.

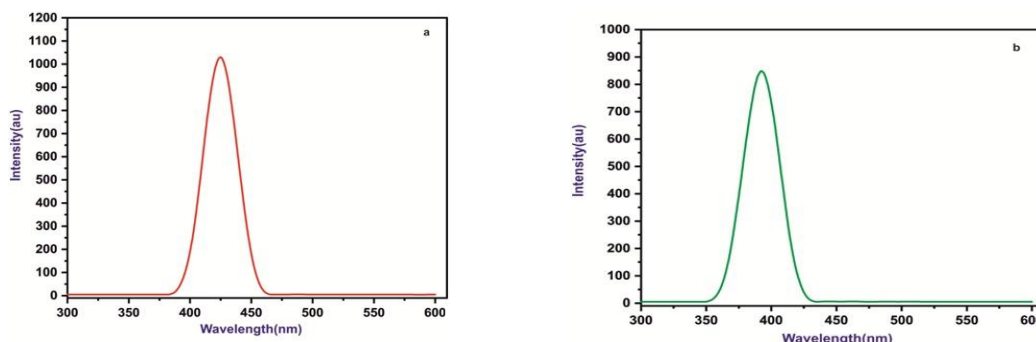


Figure 4 Fluorescence spectra (a) OA + Al³⁺ blank and (b) Protective film formed on the surface of aluminium after immersion in the solution containing 250 ppm of OA + 50 ppm of Zn²⁺

3.4 Analysis of FTIR Spectra

FTIR Spectra have been used to analyze the complex formed between Inhibitor and metal ion [27-31]. The FTIR spectrum (KBr) of pure AA is shown in Figure 5 (a). The C=O extending occurrence of carbonyl cluster come out at 1556 cm⁻¹. The OH stretching occurrence come out at 3431.71 cm⁻¹. The FTIR spectrum of the layer is produced on the metallic surface after submersion in resolution including 60 ppm Cl⁻ ions, 250 ppm of AA and 50ppm Zn²⁺ is exposed in Figure 5(b). The C=O stretching frequency of carbonyl group has shifted from 1600 cm⁻¹ to 1417 cm⁻¹



¹. This observation suggests that AA has coordinated with Al^{3+} through oxygen atom of the carbonyl group resulting in the formation of Al^{3+} -AA complex. The crest emerge about 650 cm^{-1} corresponds to Zn-O stretching. The peak appears around 3440 cm^{-1} is suitable to OH^- stretching. This confirms that $Zn(OH)_2$ formed. Thus the FTIR spectrum schemes direct to the finale that protecting film obtain of Al^{3+} -AA complex and $Zn(OH)_2$ produced on metallic plane.

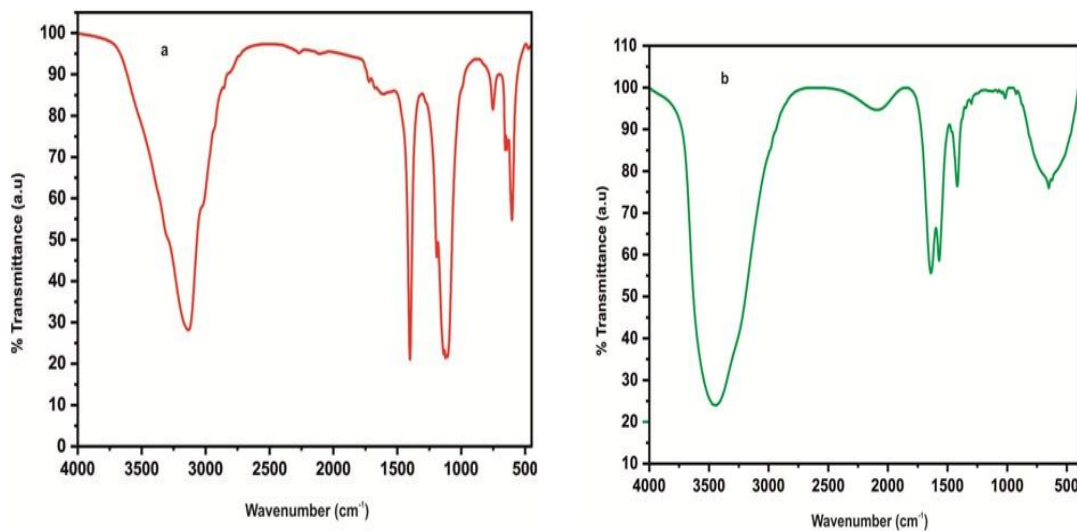


Figure 5.7 FTIR spectrum of (a) Pure AA and (b) Film formed on the metallic surface behind submersion in sedimentary resolution including 60 ppm of Cl^- ions + 250 ppm of AA + 50 ppm of Zn^{2+}

The FTIR spectrum (KBr) of pure OA is shown in Figure 5 (a). The C=O extending occurrence of carbonyl cluster come out at 1556 cm^{-1} . The OH stretching occurrence come out at 3431.71 cm^{-1} . The FTIR spectrum of the layer is produced on the metallic surface after submersion in resolution including 60 ppm Cl^- ions, 250 ppm of OA and 50 ppm Zn^{2+} is shown in Figure 6(b). The C=O stretching frequency of carbonyl group has shifted from 1556 cm^{-1} to 1375 cm^{-1} . This observation suggests that OA has coordinated with Al^{3+} through oxygen atom of the carbonyl group resulting in the formation of Al^{3+} -OA complex. The crest emerge around 600 cm^{-1} corresponds to Zn-



O stretching. The peak appears around 3500 cm^{-1} is due to OH^- stretching. This confirms that $\text{Zn}(\text{OH})_2$ formed. Thus the FTIR spectrum schemes direct to the finale that protecting film obtain of Al^{3+} -OA complex and $\text{Zn}(\text{OH})_2$ formed on metal surface.

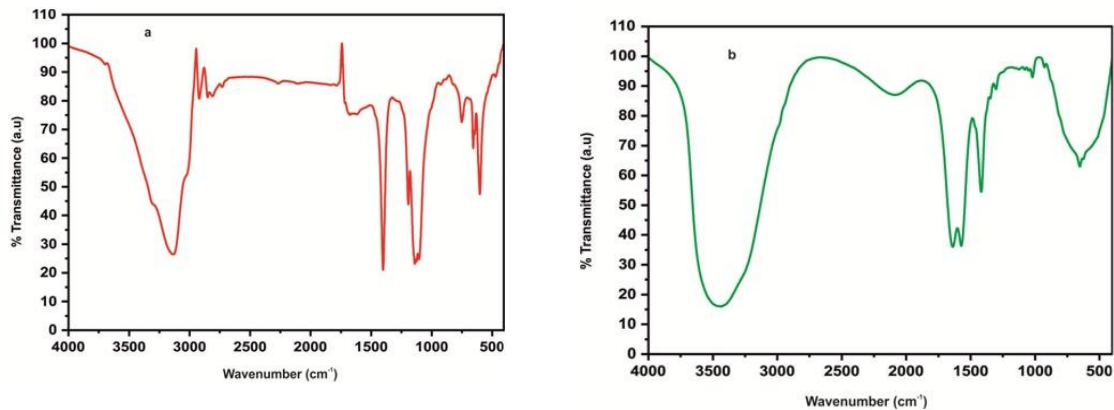


Figure 6 FTIR spectrum of (a) Pure OA and (b) Film formed on the metallic surface behind submersion in sedimentary resolution containing 60 ppm of Cl^- ions + 250 ppm of OA + 50 ppm of Zn^{2+}

Conclusions

The present study leads to the following conclusion

- The Formulation consisting of 250ppm of Oxalic acid and Adipic Acid , 50ppm of Zn^{2+} offers 95% Inhibition Efficiency of Aluminium immersed in an aqueous solution at pH 10.
- The UV-visible absorption spectrum of an sedimentary solution incorporating AA indicates that a complex in solution is formed between AA- Al^{3+} .
- Fluorescence spectra peaks indicate that there is a complex formed between AA and Zn^{2+} in the metal plane.
- FTIR reveals that the protecting layer consists of Al^{3+} -AA complex and $\text{Zn}(\text{OH})_2$ formed on metal surface.
- The UV-visible absorption spectrum of an aqueous solution containing OA indicates that a complex in solution is formed between OA- Al^{3+} .
- Fluorescence spectra peaks indicate that there is a complex formed between OA and Zn^{2+} on the metal surface.
- FTIR reveals that the protective film consists of Al^{3+} -OA complex and $\text{Zn}(\text{OH})_2$



formed on metal surface.

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