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Corrosion Inhibition by Malonic Acid

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Abstract: ***The inhibition efficiency of malonic acid is controlling corrosion of Aluminium in an aqueous solution at pH 10, in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 250 ppm of malonic acid and 50 ppm of Zn^{2+} has 90% corrosion inhibition efficiency. A synergistic effect exits between malonic acid and Zn^{2+}.The mechanistic aspects of corrosion inhibition have been studied by electro chemical studies such as polarization study and AC impedance spectra. In the presence of inhibitor linear polarization resistance increases and corrosion current decreases. The protective film formed has been analysed by FTIR spectroscopy. The protective film consists of aluminium-malonic acid complex. There is also possibility of zinc-malonic acid complex.***

Keywords: Corrosion inhibition, Aluminium at pH 10, malonic acid, polarization study, FTIR spectroscopy

1. Introduction

Aluminum is one of the metals which used in different human activities and many of important applications, where it is the second most abundant metal after iron, it has a low atomic mass and negative value of standard electron potential, aluminum potentially attracts as an anodic material for power sources with high energy density. It is used in construction, packing and transportation because of its strength and electrical conductivity. Aluminum is used in electronics due to it is super purity [1]. Although Al has an adhesive protective passivating oxide film, but this film hasan amphoteric susceptibility, and consequently the metal dissolves readily in acidic and basic solutions concentrated above and below pH 4-9 [2, 3]. Aluminum and its alloys have remarkable economic and attractive materials for engineering applications owing to its low cost, light weight, high thermal and electrical conductivity. The interest of the materials arises from their importance in recent civilization. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion media [4]. To prevent the attack of acid, it is very important to add a corrosion inhibitor to decrease the rate of Al dissolution in such solutions. Thus, many studies concerning the inhibition of Al corrosion using organic substances are conducted in acidic and basic solutions [5-9].

The present work is undertaken

- To evaluate the inhibition efficiency of malonic acid in controlling corrosion of aluminium immersed in an aqueous solution at pH 10, in the absence and presence of Zn^{2+} using the weight loss method
- To study the mechanistic aspects of corrosion inhibition by potentiodynamic polarization and AC impedance spectra

2. Methods and Materials

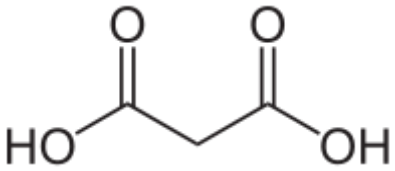
2.1 Preparation of specimens

Commercial aluminium specimens of dimensions 1.0 x 4.0 x 0.2cm, containing 95% pure aluminium were polished to mirror finish, degreased with trichloroethylene, and used for the mass-loss method.

2.2 Inhibitor solution

1g malonic acid was dissolved in double distilled water and the solution was made up to 100ml. The pH of the solution is 10 and this solution was used as a inhibitor solution

The structure of malonic acid is shown in scheme 1.



Scheme 1 – malonic acid

2.3. Weight loss method

Three aluminium specimens were immersed in 100ml of the solution at pH 10 and various concentrations of the inhibitor in the absence and presence of Zn^{2+} for a period of 1 day. The weight of the specimen before and after immersion was determined using Shimadzu balance AY62.Inhibition efficiency (IE) was calculated from the relationship.

$$IE = 100\ [1-W2/W1)]\ \%$$

Where W1 and W2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

2.4. Potentiodynamic polarization study

Polarization study was carried out in a CHI electrochemical work station impedance analyzer model 660A. A three electrode cell assembly was used. The

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working electrode was Aluminium, A saturated calomel electrode (SCE) was the reference electrode and platinium was the counter electrode. The corrosion parameters such as linear polarization Resistance. (LPR), corrosion potential, E_{corr}, corrosion current, I_{corr}, and Tafel slopes (b_a and b_c) were measured.

2.5. Alternating current impedance spectra

AC impedance spectra were recorded in the same instrument used for polarization study, using the same type of three electrode cell assembly. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance **(**C_{dl}) values were calculated.

2.6 FTlR Spectra

These spectra were recorded with the Perkin Elmer -1600 FTIR spectrophotometer. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

3. Results and Discussion

3.1. Analysis of the weight loss method

The corrosion rate of aluminium in an aqueous solution at pH 10 in the absence and presence of inhibitor obtained by weight loss method are given in Table 1. The inhibition efficiency is also given in Table-1. It is observed from Table -1 that malonic acid (MA) has good inhibition efficiency (IE).As the concentration of inhibitor increases, the inhibition efficiency (IE) also increased. As the concentration inhibitor increases, more inhibitor molecules are adsorbed on the metal surface and hence, corrosion protection increases. Corrosive ions are not able to attack the metal surface.

Table 1
Corrosion rates of Aluminium in an aqueous solution at pH 10, in the absence and presence of inhibitor system and the inhibition efficiencies (IE) obtained from weight loss method.

Inhibitor system: malonic acid (MA) and Zn^{2+}

malonic acid ppm	Zn^{2+} system ppm	Corrosion rate mdd	Inhibition efficiency %
0	0	23.48	--
50	0	6.80	71
100	0	6.33	73
150	0	5.87	75
200	0	5.40	77
250	0	5.16	78

Table 2
Corrosion rates of Aluminium in an aqueous solution at pH 10, in the absence and presence of inhibitor system and the inhibition efficiencies (IE) obtained from weight loss method.

Inhibitor system: malonicacid (MA) and Zn^{2+}

malonic acid ppm	Zn^{2+}system ppm	Corrosion rate mdd	Inhibition efficiency %
0	0	23.48	--
0	50	19.25	18
50	50	3.99	83
100	50	3.52	85
150	50	2.81	88
200	50	2.58	89
250	50	2.34	90

3.2. Influence of Zn^{2+} on the inhibition efficiency of malonic acid (MA)

The influence of Zn^{2+} on the IE of MA is given in Table 1 and 2. In the presence of Zn^{2+} (50 ppm) excellent inhibitive property is shown by MA. A synergistic effect exists between MA and Zn^{2+} For example, 250 ppm of MA has 86% IE, 50 ppm of Zn^{2+} has 13 or 18% IE. But their combination has 90% inhibition efficiency. This suggest that a synergistic effect exist between MA and Zn^{2+}

3.3. Analysis of polarization curves

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process [10-22] the potentiodynamic polarization curves of aluminium immersed in various solutions at pH 10 are shown in Figure1. The corrosion parameters such as corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (b_a, b_c) and linear polarization (LPR) are given in Table 3.

When aluminium is immersed in an aqueous solution at pH 10, the corrosion potential is -583 mV vs SCE. When the inhibitors are added, (250ppm of MA and 50ppm of Zn^{2+}) the corrosion potential shifted to anodic side (-415mV vs SCE). A shift of corrosion potential in the noble side is an indication of formation of protective film on the metal surface. Further LPR value increases from 50260 to 85826 Ohm cm^2 and corrosion current decreases from 5.226×10^{-7} A/cm^2 to 3.983×10^{-7} A/cm^2. These results suggest that a protective film is formed on the metal surface.

Table 3
Corrosion parameters of Aluminium immersed in an aqueous solution at pH 10, in the absence and presence of inhibitor system obtained from polarization study

Inhibitor system: Malonic acid (MA) and Zn^{2+}

MA ppm	**Zn^{2+} Ppm**	**E_{corr} mV vs SCE**	**bc mV**	**ba mV**	**LPR Ohm cm^2**	**I corr A/cm^2**
0	0	-583	293	284	50260	5.226×10^{-7}
250	50	-415	169	146	85826	3.983×10^{-7}

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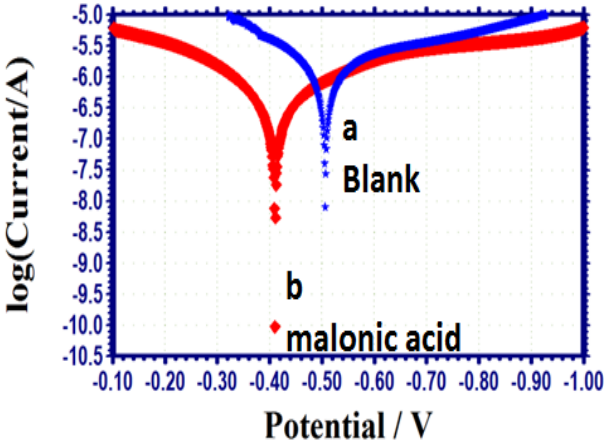


Figure 1: Polarization curves of aluminium immersed in various test solution

a)Aqueous solution at pH 10. b)In presence of 250 ppm MA + 50 ppm Zn^{2+}.

3.5. Analysis of AC impedance spectra

AC impedance spectra (electrochemical impedance spectra) have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases and double layer capacitance value (C_{dl}) decreases. The AC impedance spectra of aluminium immersed in various solutions are shown in Figure. The Nyquist plots are shown in Figure 2(a) and 2(b).The Bode plots are shown in Figure 3(a) and 3(b). The corrosion parameters such as charge transfer resistance (Rt), double layer capacitance value (C_{dl}) derived from Nyquist and Bode plots are given in Table 4.

When aluminium is immersed in an aqueous solution at pH 10, the charge transfer resistance R_t is 1.955 Ohm cm^2, the double layer capacitance $\mathbf{C_{dl}}$ is 5.950 x 10^{-8} F/cm^2. When the formulation consisting of MA and Zn^{2+} is added, the R_t, value increases and C_{dl} value decreases. This confirms that a protective film is formed on the metal surface. This decreases the corrosion rate of aluminium and increases the inhibition efficiency.

Table 4
Corrosion parameters of Aluminium immersed in an aqueous solution at pH 10, in the absence and presence of inhibitor system obtained from AC impedance spectra

Inhibiton system: malonicacid (MA) and Zn^{2+}

AA ppm	Zn^{2+} Ppm	Rt Ohm cm^2	Cdl F/ cm^2	Bode plot Impedance log(z/ohm)
0	0	85.71	$5.950x10^{-8}$	1.955
250	50	1254	$3.9876x10^{-9}$	3.635

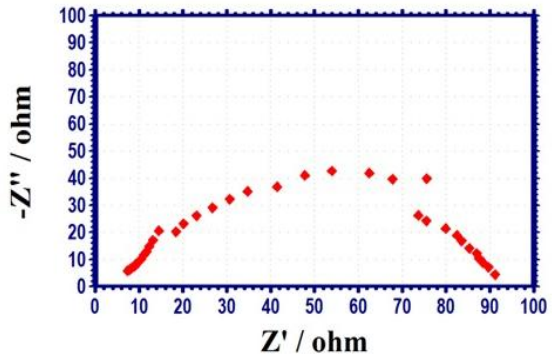


Figure 2(a): AC impedance spectra of aluminium immersed in an aqueous solution at pH 10Nyquist plot)

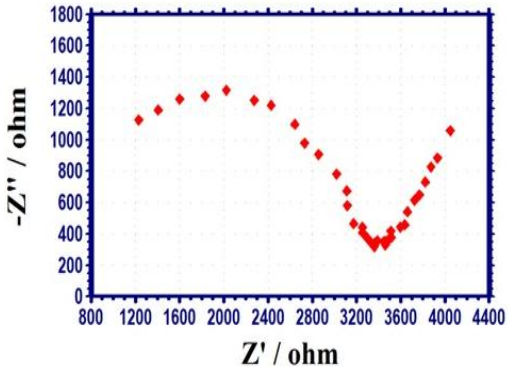


Figure 2 (b): AC impedance spectra of aluminium immersed in an aqueous solution MA 250ppm + Zn^{2+} 50ppm at pH 10(Nyquist plot)

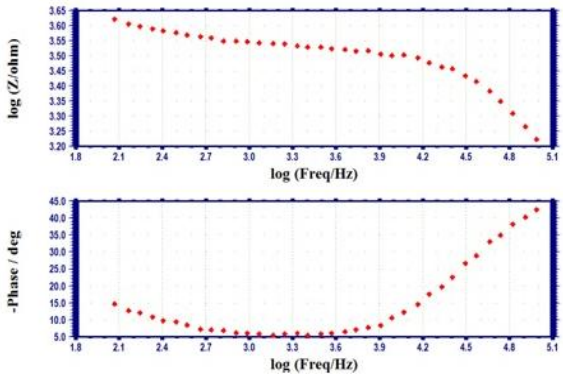


Figure 3(a): AC impedance spectra of aluminium immersed in an aqueous solution at pH 10 (Bode plot)

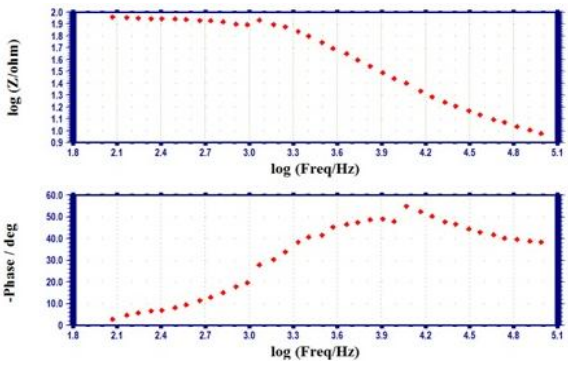


Figure 3(b): AC impedance spectra of aluminium immersed in an aqueous solution in presence of MA 250ppm+ Zn^{2+} 50ppm pH 10 (Bode plot)

3.6 Analysis of FTIR spectra

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FTIR spectra have been used to confirm the presence of protective film formed on metal surface [23]. FTIR spectra of pure melonic acid (kBr) are shown in Figure 7 (a). The peak appears at 1641.1cm^{-1} is due to the CO stretching frequency of the carbonyl groups. The OH stretching frequency of the carboxyl groups appears at 3437.0 cm^{-1}.The aliphatic CH stretching frequency appears at 2923.3 cm^{-1}h. Thus melonic acid is confirmed by FTIR spectra. The FTIR spectra (kBr) of the protective film formed on the metal surface after immersion in the solution containing 250ppm of malonic acid and 50ppm of Zn^{2+} is shown in Figure7 (b). Its observed that CO stretching frequency has shifted from 1629.3cm^{-1} to1641.4cm^{-1}.The OH stretching frequency has shifted from 3431.9 cm^{-1}to 3450.8 cm^{-1}.This suggest that melonic acid has coordinate with Al^{3+} on the metal surface through carbonyl oxygen atom of carboxyl groups. The peak at 673.9 is due to a Metal –Oxygen bond[M-O].The peak at 3450.8 cm^{-1} is due to OH groups. This indicates that there is possibility of zinc hydroxide and /or aluminum hydroxide on metal surface. Thus if analysis of FTIR spectra leads to the conclusion that the protective film consist of Al^{3+} /Al complex and zinc hydroxide. There is also possibility of formation of aluminium hydroxide on the metal surface.

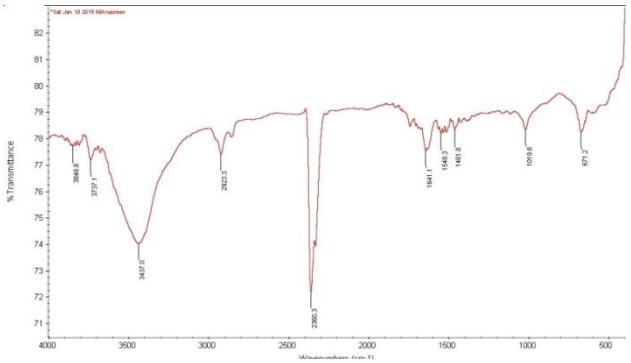


Figure 7(a): FTIR spectrum of Malonic acid

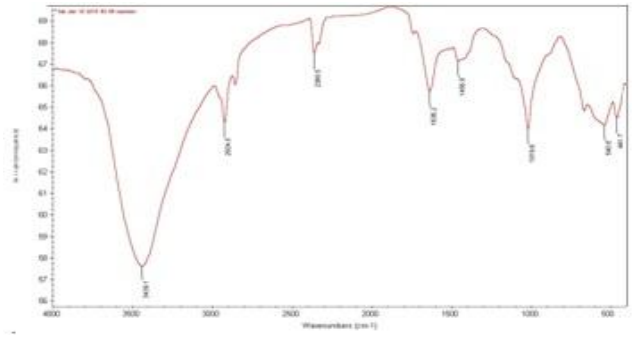


Figure 7(b): FTIR spectrum of film formed on metal surface after immersion in solution containing MA 250ppm+ Zn^{2+} 50ppm

4. Conclusion

The present study leads to the following conclusion

- The Formulation consisting of 250ppm of malonic acid and 50ppm of Zn^{2+} offers 95% inhibition efficiency of aluminium immersed in an aqueous solution at pH 10;
- Polarization study reveals that the composition of 250 ppm MA and 50 ppm Zn^{2+} function as the anodic inhibitor;
- AC impedance spectra reveals that a protective film formed on the metal surface;
- FTIR spectra reveal that the protective film consists of Al^{3+} /Al complex and $Zn(OH)_2$

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