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ELECTROCHEMICAL AND SURFACE ANALYSIS STUDIES ON CORROSION INHIBITION OF ALUMINIUM BY AN ECO-FRIENDLY INHIBITOR IN ALKALINE MEDIUM

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Abstract

The goal of studying the processes of corrosion is to find methods of minimizing or preventing it. One approach is the use of corrosion inhibitors. Although many synthetic compounds show good anticorrosive activity, most of them are highly toxic to both human beings and the environment and they are often expensive and non-biodegradable. Thus, the use of natural products as corrosion inhibitors has become a key area of research because plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that are biodegradable in nature and can be extracted by simple procedures with low cost. This research aims to study the corrosion inhibition behavior of different concentrations of Basella Alba leaf extract as an inhibitor for the corrosion of Aluminium metal in the alkaline medium using weight loss study, thermometric method, electrochemical studies and surface examination technique. The results showed that the percentage inhibition efficiency (IE) increased up to a particular concentration of the plant extract (PE) then it decreased. The highest IE 97% was obtained with 8 ml of PE in 0.5N NaOH. The polarization data revealed that PE acts as a cathodic inhibitor. Adsorption of extract on the Aluminium surface obeyed Langmuir adsorption isotherm. The thermodynamic parameters were calculated and discussed. The protective film formed on the metal surface by the adsorption of inhibitor was confirmed using Scanning Electron Microscopy (SEM) studies.

Keywords - Aluminium; Corrosion; Electrochemical techniques; SEM

1. Introduction

Corrosion results in destroying the lusture and beauty of the objects. By using suitable inhibitors it can be controlled. Corrosion inhibitors are those compounds when added to the corroding environment delays the phenomenon of corrosion [1]. The

inhibitors contain a number of heteroatoms like oxygen, sulphur, nitrogen etc. in their structure. The inhibitors control corrosion by simply blocking the active sites of the metal surface [2]. The aim of using the inhibitor is to reduce the corrosion rate [3]. Aluminium, the lightest of the known metals has been used extensively to make machinery and aircraft parts. Aluminium gets corroded very easily in the alkaline medium when compared with the other media with profuse hydrogen evolution [4].

2. Experimental method

2.1. Preparation of the specimen

Aluminium metals of dimensions 1.0 cm x 4.0 cm x 0.1 cm containing 1.5% Pb, 0.1% Ga, 1% In and the remainder Al were mechanically polished to a mirror finish and degreased with acetone. They were used for the weight loss method and surface examination studies.

2.2. Preparation of the leaf extract (PE)

Basella Alba leaves were collected and dried under shade and an aqueous extract of it was prepared by refluxing 5 g of it with double distilled water for 3 hours, cooled, filtering the suspended impurities and making up to 200 ml. The extract was used as corrosion inhibitor in the present study.

2.3. Weight-loss method

The weight loss technique is the conventional and simplest of all corrosion techniques. Aluminium metals were completely immersed in 100 ml of the test solution (0.5 N, 0.3 N and 0.1 N NaOH) containing various concentrations of the inhibitor (PE) for a period of 3 hours. The weights of the specimen before and after immersion were determined using a digital balance. The corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100[1 - (W_2/W_1)] \%$$

W_1 and W_2 are the corrosion rate in the absence and in the presence of the inhibitor. Corrosion rate is calculated assuming uniform corrosion over the entire surface of the coupon. Corrosion rates (CR) are calculated from weight loss method using the formula

$$CR = 534 W / DAT \text{ Mills per year (mpy)}$$

where, W = weight loss in milligrams, D = density of specimen g/cm^3 , A = area of specimen in square inches, T = exposure in hours.

2.4. Potentiodynamic Polarization

Polarization studies were carried out in a CHI electrochemical work station with impedance model 608 E. A three – electrode cell assembly was used. The working electrode was Aluminium metal. A SCE was the reference electrode. Platinum is used as the counter electrode. Both cathodic and anodic polarization curves were recorded in the absence and presence of the plant extract. From polarization studies, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic (β_a) and cathodic (β_c) were calculated and a linear polarization study was done. The scan rate (V/S) was 0.01. Hold time at E_f (s) was zero and quiet time (s) was two.

2.5. Scanning Electron Microscope

The nature of the film formed on the exterior of the Aluminium metal surface was analysed using SEM. The surface analysis of the polished Aluminium metal and the same in inhibited and uninhibited environment was investigated. Aluminium specimens were immersed in blank and in the inhibitor solutions for a period of 3 hours. The specimens were taken out rinsed with double distilled water, dried and witnessed under scanning electron microscopy to observe the surface morphology.

3. Results and Discussion

3.1. Weight Loss Study

Corrosion inhibition efficiencies (IE%) and the corresponding corrosion rates (CR) in mils per year (mpy) of PE in alkaline solution (0.5N, 0.3N, 0.1N NaOH) have been explained below.

The weight loss study was carried out without and with the inhibitor. The concentration of the inhibitor was varied from 2 ml to 10 ml. Their corresponding IE and CR are tabulated in Table 1. It was observed that 8 ml of PE showed 97% IE in 0.5N NaOH when compared with other systems. Hence this system was chosen as the best system for further studies. The results also indicate that as the IE increases the CR decreases. Hence it shows that the PE acts as a potent inhibitor for the corrosion of Aluminium in various alkaline solution [5,6].

Table 1: Corrosion inhibition efficiency (IE) and the corresponding corrosion rates (CR) in mills per year (mpy) of Aluminium in various alkaline solutions in the absence and presence of PE

PE in ml	0.5N NaOH		0.3N NaOH		0.1N NaOH	
	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)
0	0	1722.3	0	1465.0	0	1079.0
2	52	1238.5	68	986.2	56	603.24
4	63	1120.8	75	729.6	64	385.07
6	82	912.8	82	588.2	77	295.50
8	97	882.6	91	525.2	85	250.17
10	85	918.9	72	736.0	50	635.70

3.2. Thermometric Study

Fig. 1 shows the plot of temperature versus time for the corrosion reaction of Aluminium in NaOH in the absence and presence of different concentrations of PE. Inspection of the figure revealed that the dissolution of Aluminium starts after a certain time from the immersion of the Aluminium metals in the test solution as evident in the constant temperature with time. It may be expected that this time corresponds to the period required by the alkali to destroy the pre-immersion oxide film and is known as the 'incubation period'. After the consumption of the pre-immersion oxide film, the temperature of the system rises gradually due to the exothermic corrosion reaction to reach a maximum value T_m .

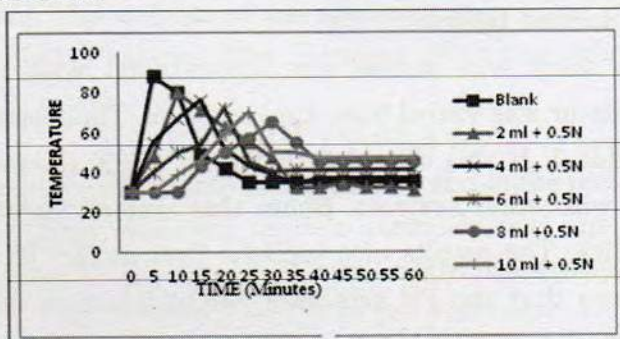


Figure 1: Temperature - Time curves for Aluminium corrosion in 0.5N NaOH in the presence and absence of PE of different concentrations

It is seen from Fig. 1 that the maximum temperature T_m was attained at a very short time (t) by the free alkaline solution. This corresponds to a reaction number (RN) of $20.44^\circ\text{C min}^{-1}$ (Table 2). Further inspection of Fig. 1 revealed that on addition of the PE the maximum temperature attained decreased and the time required reaching it increased correspondingly. This is an indication that the various additives inhibit the corrosion of Al in the alkaline environment, probably by adsorption of the metal surface [7]. The extent of inhibition depends on the degree of coverage of the metal by the adsorbed molecules. Strong adsorption is noted at 8 ml of PE as depicted by further decrease in maximum temperature (T_m) attained and a corresponding increase in time (t) taken to reach it, and both factors cause a large decrease in the RN of the system (Table 2). The temperature of all the systems decreased after reaching their maximum values. This could be attributed to decreasing corrodent concentration with increasing reaction time. The rate of adsorption decreases after 8 ml of the PE. This may be due to the fact that the protective film is unstable at higher concentrations. A maximum decrease in quantity of heat evolved is observed with 8 ml of PE compared to 10 ml of PE. The results obtained in this study corroborate those of other studies [8,9].

Table 2: Calculated values of Reaction Number and inhibition efficiency for Al dissolution in 0.5N NaOH containing PE

PE in ml	0.5N NaOH	
	Inhibition Efficiency (IE %)	Reaction number (RN)
Blank	0	20.44
2	62.05	12.59
4	76.69	7.30
6	82.09	4.58
8	92.55	2.05
10	87.37	2.98

Table 2 shows the calculated values of reaction number (RN) and the percentage reduction in reaction number (inhibition efficiency) for the various systems. It is very clear from the table that reaction number decreased in the presence of PE compared to the blank solution. Also, the percentage reduction in reaction number increased with

increase in concentration of PE. This statement is also corroborated by weight loss measurements.

3.3. Effect of Temperature

The effect of temperature on the CR of Aluminium in free alkaline and in the presence of different concentration of the inhibitor was studied in the temperature range of 313K to 323K for an immersion period of 5 hours. The value of IE, CR and the surface coverage (θ) are tabulated in Table 3. It can be seen that the rate of corrosion increases with rise in temperature. However the CR is much decreased for the uninhibited solution than the inhibited solution. The decrease in the CR for the uninhibited species is the result of the mitigating effect of the PE on the metal specimens [10]. As the temperature was increased from 313K to 323K, the inhibition efficiency was found to decrease, this shows that the adsorption of PE on the metal surface may be due to physical adsorption [11]. The high surface coverage data also implies that the adsorption of PE at the Aluminium interface may be due to the electrostatic force between the atoms on the metal surface and the adsorbate (inhibitor molecules) [12,13]. By plotting the values of C/θ values versus C , straight line graph was obtained (Figure 2), which showed that Langmuir adsorption isotherm is obeyed.

Table 3: Effect of Temperature on the IE of the PE in 0.5N NaOH

PE in ml	313K			323k		
	IE (%)	θ	CR (mpy)	IE (%)	θ	CR (mpy)
0	68	0.68	1145.08	64	0.64	1378.12
2	77	0.77	880.71	71	0.71	977.46
4	84	0.84	738.79	79	0.79	771.19
6	89	0.89	656.52	83	0.83	639.08
8	94	0.94	616.12	90	0.90	574.17

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm was related to the equation:

$$C_{inh}/\theta = 1/K_{ads} + C_{inh}$$

Where K_{ads} is the adsorption constant.

C is the concentration of the inhibitor

θ is the degree of surface coverage of the inhibitor

The plot of C_{inh} versus C/θ of PE give the Langmuir Adsorption isotherm, which is shown in figure 2. From the plot it was observed that there exists a linear relationship. The linear correlation coefficient, r^2 value was found to be closer to 1 in 0.5N NaOH. This confirms the adsorption of PE on the metal surface. The plot of straight lines indicates the formation of monolayer adsorbate on the adsorbent [14,15].

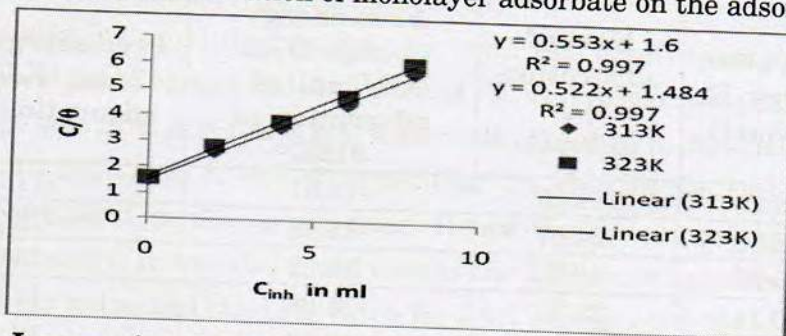


Figure 2: Langmuir adsorption isotherm plotted as “C/θ” versus “C” for Aluminium corrosion in 0.5N NaOH containing various concentrations of PE at 313 K & 323 K

3.4. Thermodynamic Parameters

The calculated values of apparent activation energy (E_a), heat of adsorption (Q_{ads}), and free energy adsorption (ΔG_{ads}) of different concentrations of the PE are shown in Table 4. The results show that the apparent activation energy E_a , increases as inhibitor concentration increases. Activation energy of PE ranged between 78.23 and 101.25 KJ/mol. Since corrosion primarily occurs at surface sites free of adsorbed inhibitor, the higher E_a values in inhibited solutions imply that extracts mechanically screen the active sites of Aluminium surface thereby decreasing the surface area available for corrosion [16,17].

The heat of adsorption, Q_{ads} were all negative and ranged from -14.06 to -43.71 KJ/mol for PE. The negative Q_{ads} value indicates adsorption and hence inhibition efficiency decreases as temperature increase, supporting the earlier proposed physisorption mechanism.

The free energy adsorption ΔG_{ads} , were all negative in the temperatures under study. This indicates the adsorption of inhibitor on the surface of Aluminium, and it was proposed that it may be physical adsorption ($\Delta G_{ads} < 40$ KJ/mol) [18]. Generally, values of ΔG_{ads} around -20KJ/mol or less negative are consistent with physisorption while those around -40 KJ/mol or more negative values involve chemisorptions [19].

Table 4: Thermodynamic parameters for the corrosion of Aluminium in 0.5N NaOH at different temperatures

PE in ml	Activation energy, E_a (KJ/mol)	Heat of adsorption Q_{ads} (KJ/mol)	Free energy change ΔG_{ads} (KJ/mol) of adsorption at 313K	Free energy change ΔG_{ads} (KJ/mol) of adsorption at 323K
0	78.23	-14.06	-12.01	-11.95
2	78.56	-24.67	-13.16	-12.78
4	85.76	-26.28	-14.29	-13.90
6	90.14	-39.83	-15.38	-14.58
8	101.25	-43.71	-17.05	-16.17

3.5. Analysis of Polarization Curves

Figure 3 shows the anodic and cathodic polarization curves for Aluminium in 0.5N NaOH with and without various concentrations of PE. The numerical values of potentiodynamic parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (β_a and β_c) and linear polarization resistance (LPR) are given in Table 5.

Table 5: Corrosion parameters of Aluminium in 0.5N NaOH solution in the absence and presence of various concentrations of the inhibitor obtained by polarization methods

PE in ml	E_{corr} V VS SCE	I_{corr} A/cm ²	β_a (v/dec ⁻¹)	β_c (v/dec ⁻¹)	LPR
0	-1.317	5.012×10^{-7}	5.264	5.316	40
2	-1.362	7.045×10^{-7}	4.176	5.141	60
4	-1.318	1.624×10^{-8}	4.617	6.064	77
6	-1.317	3.716×10^{-8}	6.716	7.911	96
8	-1.311	8.04×10^{-8}	9.441	12.146	23x10
10	-1.312	2.51×10^{-8}	11.117	14.912	13x10 ⁴

3.6. Surface Analysis

Scanning Electron Microscope (SEM) was used for the surface examination of the Aluminium species. The Aluminium species before and after immersion in the absence and presence of the inhibitor for a period of 5 hours were taken out, washed carefully with distilled water, dried and kept in desiccator. The SEM micrographs of the examined surfaces are shown in figure 4 (a, b, c). the SEM micrograph of the polished Aluminium metal surface was shown in figure 4 (a).It shows the smooth surface of the metal and absence of any corrosion products on the surface of the metal. The SEM micrograph of the Aluminium metal surface immersed in 0.5N NaOH was represented in figure 4 (b). It can be observed that the surface was strongly damaged as a result of the attack of the corrosive solution in the absence of the inhibitor.

Figure 4 (c) represents the surface analysis of the Aluminium metal immersed in 0.5N NaOH in the presence of 8 ml PE. The analysis showed that the metal surface immersed in the inhibitor solution was in better condition, having smooth surfaces compared with surface of the sample immersed in 0.5N NaOH. This improvement in surface morphology is due to the formation of a good protective film which was responsible for the inhibition of corrosion [24-26]

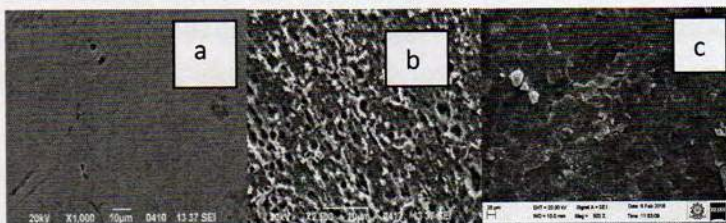


Figure 4: SEM micrographs of

(a) Polished Aluminium metal (control)

(b) Aluminium metal immersed in 0.5N NaOH

(c) Aluminium metal immersed in 0.5N NaOH containing 8 ml of PE

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