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Anionic Effect on the Acidic Corrosion of Aluminum and its Inhibition by Lupine Extract

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Abstract

Corrosion behavior of aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions was studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results showed that the rate of corrosion of aluminum was arranged in the order: HCl > $HClO_4$ > H_2SO_4**.** Lupine extract is an effective green inhibitor for the corrosion of aluminum in acidic solutions. The inhibition efficiency of the extract was found to increase with increasing the concentration of the extract. The obtained results showed that the lupine extract is effective in the order $HClO_4$ > HCl > H_2SO_4. Theoretical fitting of the corrosion data to the Kinetic-thermodynamic model was tested to clarify the nature of adsorption.

Keywords: Corrosion, acidic, aluminum, lupine, adsorption.

Introduction

Aluminum is a reactive metal [1]; aluminium and aluminium alloys are extensively used in industry in a variety of aggressive aqueous environments covering a wide range of pH. Aluminum is usually protected by a thin oxide film, whose solubility is negligible in neutral solutions (pH interval 4.0–8.5) at room temperature provided the solution does not contain activating anions, whereas heavy corrosion is observed both in acidic and alkaline media [2]. Anodizing in sulfuric acid solution can produce the protective oxide layer [3].

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The presence of chloride ions in the solution has some disadvantages like producing pitting in oxide film [4]. One of the most common methods to protect metals against acid corrosion is the use of inhibitors which reduce the corrosion rate of metals and alloys in contact with aggressive environment. Organic inhibitors are often used to protect metallic materials against corrosion in acidic as well as in alkaline media. It is generally agreed that adsorption of organic molecules at the Al – solution interface can lead to corrosion inhibition either by physically blocking the surface active sites or by retarding the electrochemical reactions [5]. The inhibition effect of some amino acids (alanine, leucine, valine, proline, methionine, and tryptophan) towards the corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 solution was investigated using weight loss measurement, linear polarization and SEM techniques [6]. The inhibition of three ethoxylated fatty acids of different molecular weights on the corrosion of aluminum in both 1.0 M HCl and 1.0 M H_2SO_4 solutions has been studied at different temperatures (25–55 °C) by means of weight loss and potentiodynamic polarization techniques. The inhibition efficiency for the three fatty acids increases with the increase in the inhibitors concentration but decreases with increasing temperature [7]. Most of the corrosion inhibitors are synthetic chemicals which are expensive and very hazardous to environment [8]. There has been increasing search for green corrosion inhibitors; inhibitors in this class are those that are environmentally friendly and are gotten from natural products such as plant extracts. This area of research is of much importance because in addition to being inexpensive, they are readily available and renewable sources of materials. Plant products are organic in nature and some of their constituents including tannins, organic and amino acids, alkaloids and pigments are known to exhibit inhibiting action [9]. Therefore, it is desirable to source for environmentally safe inhibitors, which have been found to generally exhibit good inhibition efficiencies. Pectin, which is a natural polymer, is a successful corrosion inhibitor on the surface of aluminum metal in acidic media [10]. The inhibition effect of Jasminum Nudiflorum Lindl Leaves extract (JNLLE) on the corrosion of aluminum in 1.0 M HCl solution was studied by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscopy (SEM) methods [11].

The aim of this work is to investigate the anionic effect on the acidic corrosion of aluminum and its inhibition by lupine extract.

Experimental

Electrochemical tests

Electrochemical impedance and polarization curve measurements were achieved using an ACM 604 Instrument. The frequency range for EIS measurements was $0.01 \leq f \leq 3 \times 10^4$ Hz with an applied potential signal amplitude of 10 mV around the rest potential. Polarization curve measurements were carried out at the scan rate 20 mV/min. The data were obtained in a three electrode mode; graphite rod and saturated calomel electrode were used as counter and reference electrodes. The specimens used for constructing the working electrode were aluminum rods that had the following chemical composition (wt %): Al 99.687; Mn 0.001; Zn 0.001; Ni 0.001; Ti 0.003; Fe 0.171; Si 0.135; Cu 0.001. The aluminum samples were fixed in poly tetrafluoro ethylene (PTFE) rods by an epoxy resin in such a way that only one surface was left uncovered. The exposed area (0.786 cm^2) was mechanically polished with a series of emery papers of variable grades; the samples were then washed thoroughly with distilled water followed by A.R. ethanol and finally with distilled water, just before insertion in the cell. Measurements were done at 30 ºC.

Plant and preparation of the plant extract

These items were discussed in our recent work [12].

Preparation of the test solutions

Prior each experiment, 1.0 M $HClO_4$, 1.0 M HCl or 0.5 M H_2SO_4 are added to an appropriate volume of the stock solution of the lupine extract and double distilled water to obtain solutions of 0.1 M $HClO_4$, 0.1 M HCl and 0.05 M H_2SO_4 and the required concentration of the extract.

Results and discussion

Corrosion of aluminum in the aqueous acidic solutions

Fig. 1 represents the potentiodynamic polarization curves for aluminum in the three studied mineral acids at 30 °C. The polarization curves show Tafel behavior. In presence of HCl, the active region is followed by break down potential E_b; this behavior has been previously reported by several authors [13, 14] and has been explained on the basis of the pitting corrosion of aluminum. The potentiodynamic polarization parameters for aluminum in different mineral acids at 30 °C are presented in Table 1.

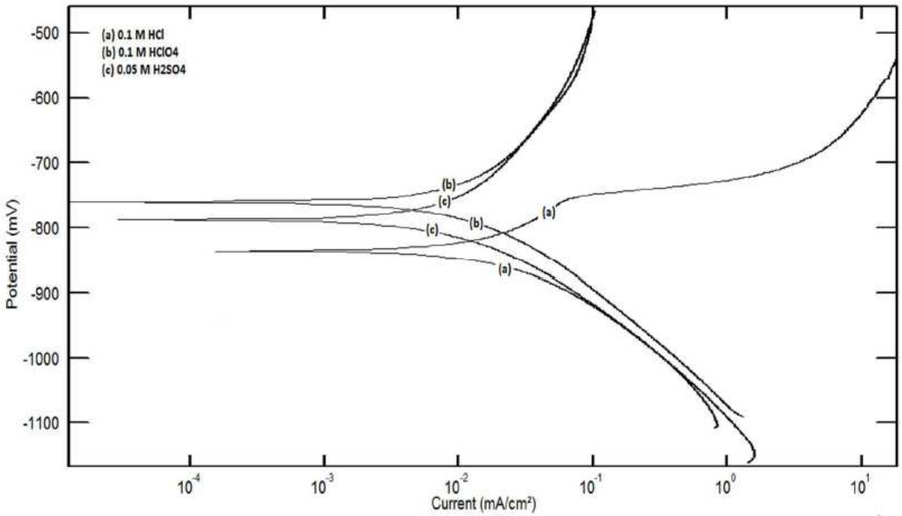

Figure 1. Potentiodynamic polarization curves for aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions at 30 ºC.

Fig. 2 represents the Nyquist plots for aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4. These plots indicate that the impedance response consisted of depressed capacitive semicircle. The experimental data were analyzed by fitting the data to the equivalent circuit model represented in Fig. 3, using Zsimpwin program. This equivalent circuit includes the solution resistance R_s shorted by the capacitor C_{dl} which is placed in parallel to the charge transfer resistance R_{ct}. The data obtained are presented in Table 2.

Table 1. Values of the polarization parameters for aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions at 30 ºC.

Type of acid	**E_{corr} (mV)**	**β_a mV/decade**	**β_c mV/decade**	**i_{corr} ($mA.cm^{-2}$)**
HCl (0.1 M)	-792.7	136.8	203.6	0.0339
$HClO_4$ (0.1M)	-774.0	375.8	201.8	0.0229
H_2SO_4 (0.05M)	-769.9	298.0	173.5	0.0155

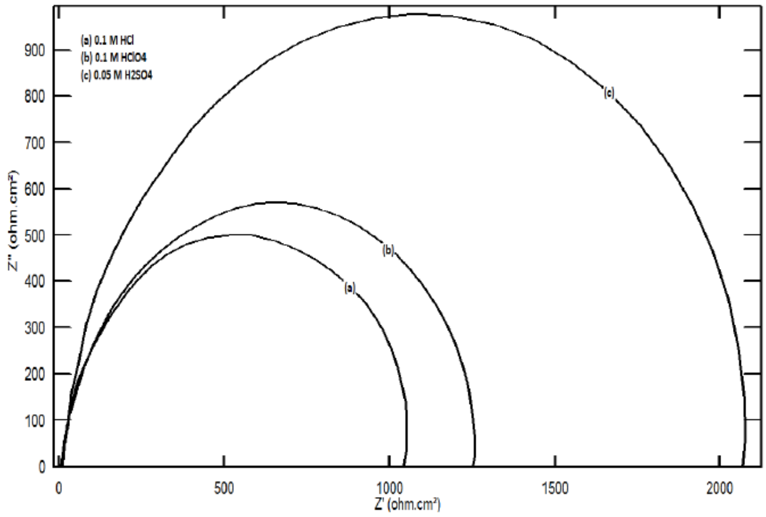

Figure 2. Nyquist plots for aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions at 30 ºC.

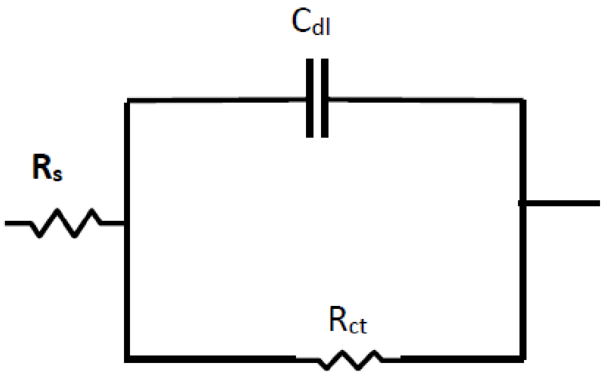

Figure 3. The equivalent circuit model.

The results showed that R_{ct} is arranged in the order: HCl < $HClO_4$ < H_2SO_4; these results are in agreement with the results obtained from the potentiodynamic polarization technique and also with the results obtained previously [15] using the gasometry technique. It has been reported that the addition of Cl^- ions increases the anodic dissolution rate of aluminum either by incorporation of the Cl^- ion into the oxide film, by which additional charge carriers are generated [16], or by the participation of Cl^- ions in the metal dissolution reaction [17,18]. In our previous work [19], the action of Cl^- ions as an accelerator has been explained on the basis of ionic incorporation into a surface film which depends upon ionic size. Consequently Cl^- ions, by their small size, can be easily incorporated. However, the bulky size of ClO_4^- and SO_4^{2-} anions would not allow their incorporation and consequently little effect would be expected on the corrosion behavior of aluminum metal. The double negative charge on SO_4^{2-} anion makes it weaker incorporated and consequently makes it the least to affect the corrosion behavior of aluminum metal. In other words, the higher values of R_{ct} in the case of sulfate ions can be explained on the basis of the formation of a binuclear surface complex [15].

Table 2. The values of the impedance parameters for aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions at 30 ºC.

Type of acid	R_s Ohm.cm^2	C_{dl} µF.cm^{-1}	R_{ct} Ohm.cm^2
HCl (0.1 M)	07.57	13.53	1006
$HClO_4$ (0.1M)	11.26	09.96	1186
H_2SO_4 (0.05M)	12.10	10.05	1967

Corrosion of aluminum in acidic solutions containing lupine

Fig. 4 represents Nyquist plots for aluminum in 0.1 M $HClO_4$ solution in the absence and presence of different concentrations of Lupine extract. The figure manifested only one depressed capacitive semicircle. The diameter of the semicircle increases with increasing the extract concentration. The percentage inhibition was calculated from impedance measurements using the relation:

$$\% \text{ inh.} = [(R_{ct} - R_{ct0}) / R_{ct}] \times 100$$

where R_{ct0} and R_{ct} are the charge transfer resistances in the absence and presence of different concentrations of the extract. Similar results obtained for aluminum in 0.1 M HCl and 0.05 M H_2SO_4 solutions in absence and presence of lupine extract.

The values of the electrochemical parameters obtained from EIS for aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions containing different lupine extract concentrations and the inhibition efficiency are given in Table 3. It is clearly seen that the presence of lupine extract enhances the values of R_{ct} and reduces the C_{dl} values. The decrease in C_{dl} is due to the adsorption of the extract to form an adherent film on the metal surface [20].

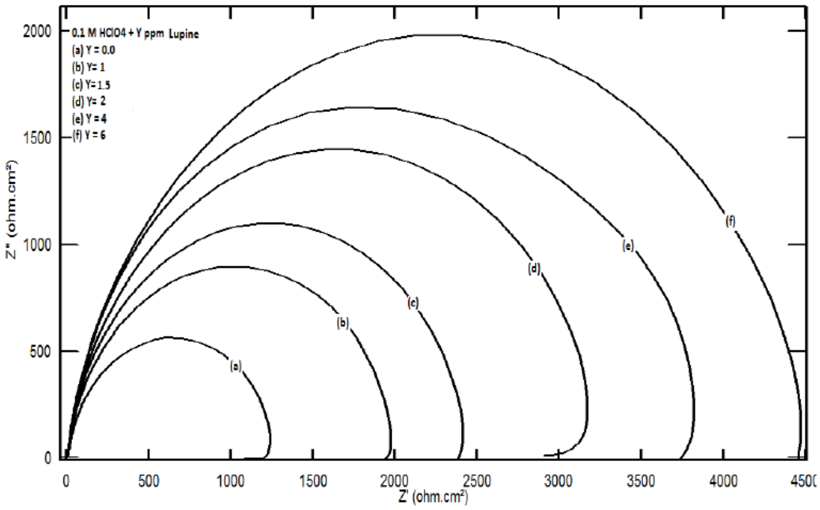

Figure 4. Nyquist plots for aluminum in 0.1 M $HClO_4$ in presence of different concentrations of lupine extract at 30 ºC.

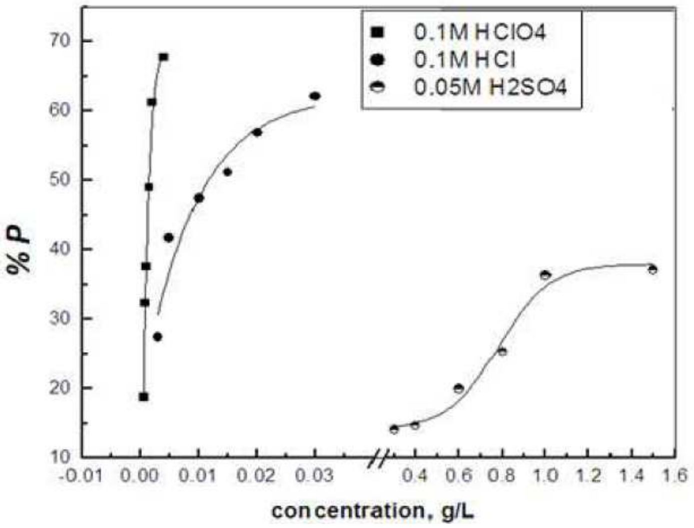

Figure 5. Variation of the percentage inhibition of aluminium in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions with concentration of lupine extract.

The variation of the percentage inhibition with concentration of lupine extract is shown in Fig. 5. These curves represent adsorption isotherms that are characterized by first sharp rising part followed by another gradual rising part indicating formation of a monolayer adsorbed film on the aluminum surface [21]. The figure also confirms the fact that the inhibition action of lupine extract for aluminum corrosion in acid medium is in the order: $HClO_4 > HCl > H_2SO_4$.

Application of the kinetic-thermodynamic model

The Kinetic-Thermodynamic model [22] is given by:

$$\log [\theta/(1-\theta)] = \log K' + y \log C$$

where y is the number of inhibitor molecules occupying one active site. The binding constant K is given by

$$K = K'(1/y).$$

Table 3. Impedance parameters for aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 in presence of different concentrations of lupine extract at 30 ºC.

Conc. (ppm)	**R_s Ohm.cm^2**	**C µF.cm^{-1}**	**R_{ct} Ohm.cm^2**	**% P**
		0.1 M HCl		
0.0	7.57	13.53	1006	
2	7.79	9.15	1225	17.9
3	7.24	11.18	1387	27.5
5	6.71	10.46	1728	41.8
10	6.66	10.12	1913	47.4
15	6.62	9.95	2060	51.2
20	6.82	9.77	2333	56.9
30	6.90	9.40	2657	62.1
50	6.84	9.71	2966	66.1
70	7.08	9.53	3259	69.2
80	6.91	8.94	3572	71.9
100	6.92	9.48	3514	71.4
		0.1 M $HClO_4$		
0.0	11.31	9.84	1186	
0.5	8.39	9.65	1461	18.8
0.75	7.20	9.37	1755	32.4
1	7.50	8.94	1903	37.7
1.5	7.64	9.18	2330	49.1
2	11.01	9.04	3066	61.3
4	9.03	8.27	3684	67.8
6	9.36	8.48	4266	72.2
7	8.44	8.47	4606	74.3
8	13.78	8.34	5075	76.6
		0.05 M H_2SO_4		
0.0	11.95	10.32	1983	
300	12.94	9.243	2310	14.2
400	14.23	9.925	2325	14.7
600	12.06	9.724	2478	20.0
800	16.64	7.146	2656	25.3
1000	13.9	8.279	3115	36.3

Fig. 6 shows the linear fitting of lupine results according to the Kinetic-Thermodynamic model. The parameters obtained from these figures are given in Table 4. It is clear that the number of active sites occupied by a single inhibitor molecule, 1/y were nearly equal one in the presence of ClO_4^- ions indicating that the inhibitor molecule occupied only one active site. But the values of 1/y in case of Cl^- and SO_4^{2-} ions indicate that each inhibitor molecule occupies more than one active site on aluminum surface.

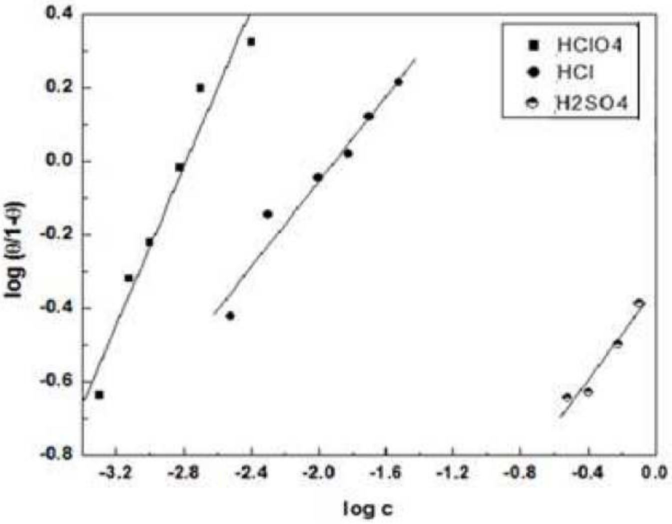

Figure 6. Application of the Kinetic-Thermodynamic model to the results of adsorption of lupine extract in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions on aluminum surface.

Since the efficiency of a given inhibitor is essentially a function of the magnitude of its binding constant K [19], the increase in the values of K in the presence of ClO_4^- ions indicates better and stronger interaction of the inhibitor molecules with the metal surface in presence of perchlorate ions. This behavior can be discussed on the basis of the low coordination ability of the perchlorate ion which tends to make the active sites of aluminum surface free and ready to adsorb the inhibitor molecules. However, the value of K is smaller in the case of SO_4^{2-} anion which can be interpreted based on the fact that the SO_4^{2-} anion is bulky and has two negative charges, and mainly coordinates with active sites of the aluminum surface; this makes it weaker to adsorb the inhibitor molecules.

Table 4. Linear fitting parameters of Lupine according to the Kinetic-Thermodynamic model for aluminum in 0.1 M HCl, 0.1 M $HClO_4$ and 0.05 M H_2SO_4.

Medium	**Model parameters**	
	Kinetic-Thermodynamic	
	1/y	**K**
$HClO_4$	0.93	613.3
HCl	1.73	80.3
H_2SO_4	1.61	0.28

Conclusions

The rate of corrosion of aluminum in aggressive mineral acid media was arranged in the order HCl > $HClO_4$ > H_2SO_4. The Cl^- ions increase the anodic dissolution rate of aluminum by their incorporation in the oxide film, however, the bulky size of ClO_4^- and SO_4^{2-} anions would not allow their incorporation. Also, the sulfate ion forms a binuclear surface complex with aluminum.

Lupine extract is effective for the acidic corrosion of aluminum in the order HClO4 > HCl > H_2SO_4.

The inhibitor molecules strongly interact with the metal surface in the presence of perchlorate ions due to the low coordination ability of the perchlorate ion; however, the sulfate ions coordinate with the metal surface makes it weaker to adsorb the inhibitor molecules.

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