

Inhibitive Action of Some Plant Extracts on the Alkaline Corrosion of Aluminum.

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The effect of extracts of Damsissa, *Corchorus itorius* on the corrosion of aluminum in aqueous 0.1M sodium carbonate were investigated by gasometry, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. EIS measurements showed that the Nyquist plots consist of capacitive semicircle followed by inductive loop indicating that the dissolution process of aluminum occurs under activation control. Potentiodynamic polarization curves indicated that the plants extracts behave as mixed-type inhibitors. Gasometry results indicated that the plants extracts retard the alkaline corrosion of aluminum. The corrosion rates of aluminum and the inhibition efficiencies of the extracts were calculated. The results obtained show that the extract solutions of the plants could serve as an effective inhibitors for the corrosion of aluminum in sodium carbonate media. Inhibition was found to increase with increasing concentration of the plants extracts. Theoretical fitting of different isotherms, Langmuir, Flory–Huggins, and the kinetic–thermodynamic model, were tested to clarify the nature of adsorption. A mechanism of the corrosion reaction of aluminum in the alkaline media was proposed.

Keywords: A. Aluminum; B. EIS; C. Gasometry; D. Polarization; E. Alkaline Corrosion.

1. INTRODUCTION

One of the most important applications of aluminum and its alloys is found in aluminum –air technology [1] Aluminum alloys are widely used in structures where a high strength to weight ratio is important, such as in the transportation industry. Aluminum has a natural corrosion protection from its oxide layer, but if exposed to aggressive environments it may corrode. Still, if correctly fabricated, constructions of aluminum may be reliable and have long service life, the known hazard effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Recently, Naturally occurring substances of both plant and animal origin which are readily available, cheap,

renewable, eco-friendly and eco-logically acceptable, have been successfully used as a replacement for the organic and inorganic inhibitors [2-5]. Plant extracts have again become important as an environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. However, synergistic (and antagonistic) effects are often expected with these mixtures of inhibitors that may affect their inhibition efficiency. Several investigations have been reported using such economic plant extracts [6-16]. They showed that the solution extract of the leaves serves as an excellent inhibitors. The existing data show that most organic inhibitors act by adsorption at the metal/solution interface. This phenomenon could take place via (i) electrostatic attraction between the charged metal and the charged inhibitor molecules, (ii) dipole-type interaction between unshared electron pairs in the inhibitor with the metal, (iii) p electrons-interaction with the metal, and (iv) a combination of all of the above [17]. The adsorption process depends on the electronic characteristics of the inhibitor, the nature of the surface, the temperature and pressure of the reaction, steric effect, multilayer adsorption and a varying degree of surface site activity.

The aim of the present work is to test extracts of Damsissa, Corchours itorius plants as inhibitors for the alkaline corrosion of aluminum and to discuss their inhibition mechanism.

2. EXPERIMENTAL

2.1. Electrochemical tests

Electrochemical impedance and polarization measurements were achieved using frequency response analyzer (FRA)/potentiostat supplied from prostate instrument. The frequency range for EIS measurements was 0.1×10^4 Hz with applied potential signal amplitude of 10 mV around the rest potential. The data were obtained in a three- electrode mode; platinum sheet and saturated calomel electrodes (SCE) were used as counter and reference electrode. The material used for constructing the working electrode was aluminum that had the following chemical composition (% wt) 99.687% Al, 0.001% Mn, 0.001% Ni, 0.001% Zn, 0.003% Ti, 0.171% Fe, 0.135% Si, 0.001% Cu was used for the electrochemical corrosion studies in aqueous solutions. The working electrode was fabricated by cutting and shaping them in cylindrical forms. A long screw fastened to one end of the test cylinder for electrical connection. The Teflon gasket thereby forms a water-tight seal with the specimen electrode that prevents ingress of any electrolyte and thus avoiding crevice effect. The leak-proof assembly exposes only glass, only one side of rod was left uncovered as constant surface area in contact with the solution. The sample was wet hand-polished using different grade emery papers 320, 400, 600, and 800 grit finishes starting with a coarse one and proceeding in steps to the fine grit up to a mirror finish, washed thoroughly with double-distilled water and finally dried by absolute ethanol, just before immersion in the solution. Each experiment was carried out with newly polished electrode. Before polarization and EIS measurements, the working electrode was introduced into the test of solution and left for 10 min to attain the open circuit potential (ocp) at which the change of ocp with time is 2

mV/min, i.e., the system had been stabilized. The polarization curve measurements were obtained at scan rate of 20mV/min starting from cathodic potential ($E_{\text{corr}} - 250$ mV) going to anodic direction. All the measurements were done at 30.0 ± 0.1 °C in solutions open to the atmosphere under unstirred conditions. To test the reliability and reproducibility of the measurements, duplicate experiments were performed in each case of the same conditions. The results were consistent within 2%.

2.2. Gasometry

Aluminum rods samples of known area were placed in Mylius sample vessel containing test solution. The vessel allows the volume of evolved hydrogen gas to be measured as a function of time. The reaction rates were determined by calculating the slope of the straight lines in the gasometry plot in absence and presence of a certain concentration of the plant extracts.

2.3. Solutions preparation

Double distilled water and Na_2CO_3 from BDH chemical company were used for preparing solutions. Stock solution of plant extracts was obtained by drying the plant for 2 h in an oven at 80° C and grinding to powdery form. A 10 g sample of the powder was refluxed in 100 mL double distilled water for 1 h. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was determining by evaporating 10 mL of the filtrate and weighing the residue. Prior each experiment, 2M Na_2CO_3 is added to an appropriate volume of the stock solution and double distilled water to obtain a solution of 0.1M Na_2CO_3 and the required concentration of the extract.

3. RESULTS AND DISCUSSION

3.1. Gasometry results

The relative rapidity and effectiveness of hydrogen evolution (gasometric) technique, as well as its suitability for monitoring in situ any perturbation by an inhibitor with respect to gas evolution in metal/corrodent systems have been established by earlier reports [18,19]. Several authors have reported on comparable agreement between gasometric technique and other techniques of corrosion monitoring. These include polarization measurement [13], weight loss [20], and thermometric technique [21]. If it is assumed that corrosion occurs only at the free sites such that the covered sites have negligible corrosion rates, the inhibition efficiency %inh. and hence the degree of surface coverage (θ) can be calculated as follows [22]:

$$\%inh = ((V_0 - V)/V_0) \times 100 \quad (1)$$

$$\theta = ((V_0 - V)/V_0) \quad (2)$$

Where V_0 and V are the corrosion rate obtained from the slopes of the gasometry plots in the absence and presence of a certain concentration of the inhibitor, respectively.

The variation of the measured volume of hydrogen gas evolved with time in 0.1 M Na_2CO_3 in absence and presence of different molar concentrations of Damsissa, Corchours itorius plants extract at 30 °C are demonstrated in figures (1,2). The volume of hydrogen gas evolved varied linearly with time. On the other hand, increasing Damsissa and Corchours itorius extracts concentration generally causes a marked decrease in that volume. This indicates that Damsissa and Corchours itorius extracts could act as inhibitors. The inhibition characteristics of Damsissa and Corchours itorius extracts might be attributed to their ability to form an adsorbed layer at the aluminum/solution interface which decreases the number of available active sites required for the alkali attack.

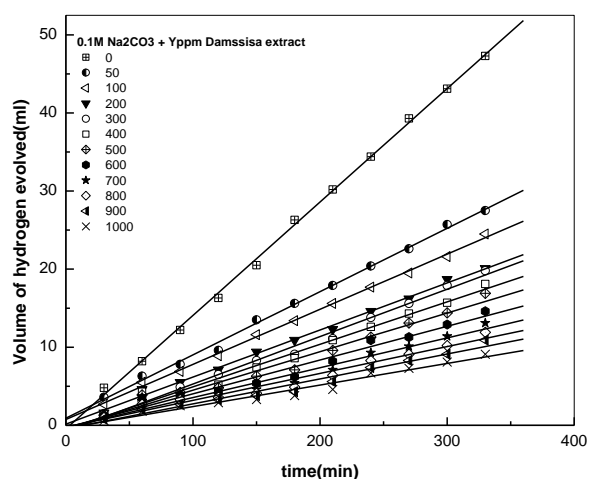


Figure 1. Plot of hydrogen evolved against time during aluminum corrosion in 0.1 M Na_2CO_3 in absence and presence of different concentrations of Damsissa extract at 30 °C.

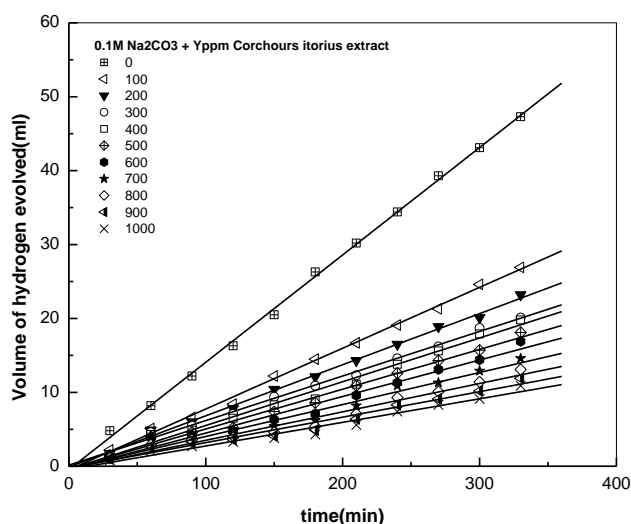


Figure 2. Plot of hydrogen evolved against time during aluminum corrosion in 0.1 M Na_2CO_3 in absence and presence of different concentrations of Corchours itorius extract at 30 °C.

Application of adsorption isotherms

The understanding of the nature of the adsorption process of various kinds of extracts on metal surface was essential to our knowledge of their inhibition action on corrosion. The action of an inhibitor in the presence of aggressive media is assumed to be due to its adsorption [23] at the metal/solution interface.

The chemical constituents of plant extracts are shown in tables (1,2). It is clear that these constituents contain oxygen, nitrogen atoms and π -electrons bonds. Therefore, the adsorption at the metal/solution interface could take place via (i) electrostatic attraction between the charged metal and the charged inhibitor molecules (ii) dipole-type interaction between unshared electron pairs in the inhibitor with the metal, (iii) the π -electrons bonds interaction with the metal, and (iv) a combination of all of the above.

Table 1. The main chemical compositions for damsissa extract.

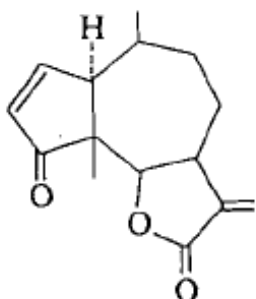
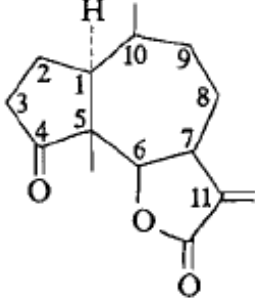
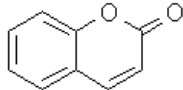
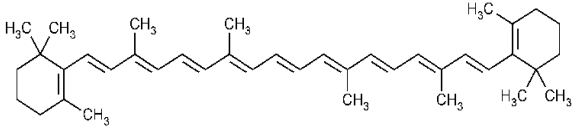
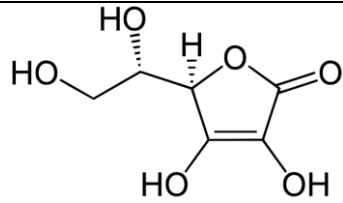
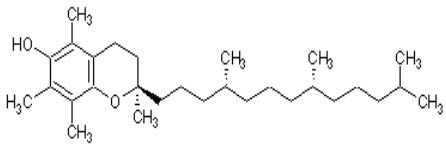
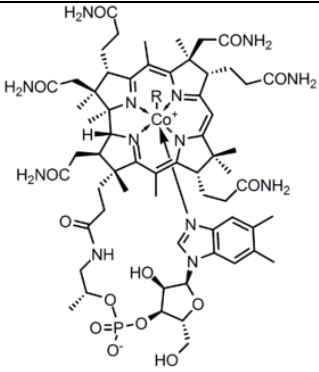
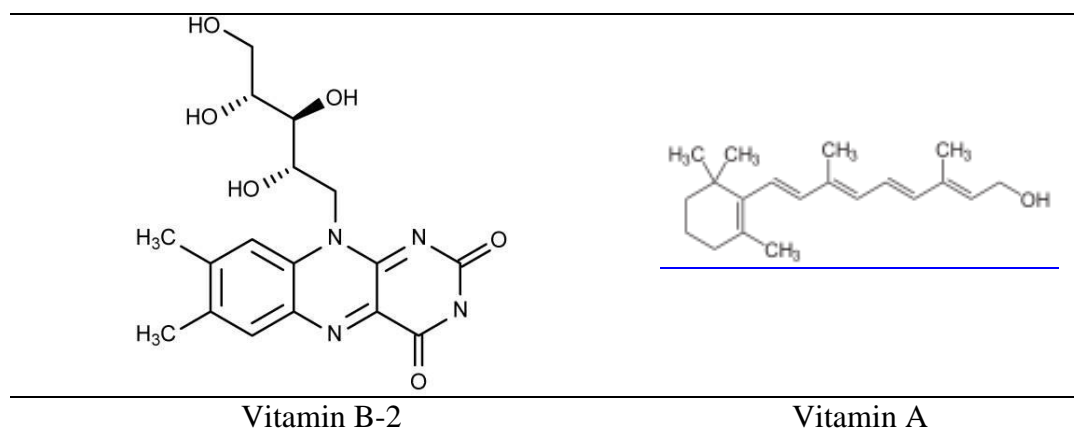
		
Ambrosin	Damsin	Coumarin

Table 2. The main chemical compositions for Corchours itorius extract.

	
Beta carotene	Vitamin C
	
Vitamin E	Vitamin B-1

R = 5'-deoxyadenosyl, Me, OH, CN



The inhibition action was regarded as simple substitutional process [24], in which an inhibitor molecule in the aqueous phase substitutes an x number of water molecules adsorbed on the metal surface, viz.



Where x is the size ratio (the relative size of the inhibitor molecule to the number of surface-adsorbed water molecules) this indicates that the number of adsorbed water molecules displaced depends on the size of the adsorbate. The degree of surface coverage (θ) of the metal surface by an adsorbed plants extract was calculated from gasometry measurements using the equation (2). The variation of surface coverage with concentration of plants extract obtained from gasometry measurements are shown in figure 3. This curve represents adsorption isotherm that are characterized by an initial steeply rising part indicating the formation of a mono-layer adsorbate films on aluminum surface.

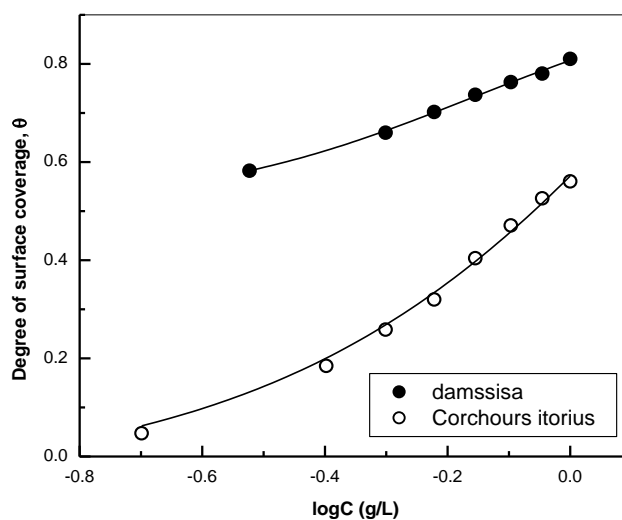


Figure 3. Variations of surface coverage with the concentration of the different extracts obtained from gasometric measurements.

Langmuir, Flory Huggins isotherms and Kinetic-Thermodynamic model were used to fit the corrosion data of the plants extract.

The Langmuir isotherm is given by [25]

$$[\theta/(1-\theta)]=K[C] \tag{4}$$

Where K is the binding constant representing the interaction of the additives with metal surface and C is the concentration of the additives.

Flory-Huggins isotherm is given by [26]

$$\theta/[x(1-\theta)^x]=K[C] \tag{5}$$

Where x is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.

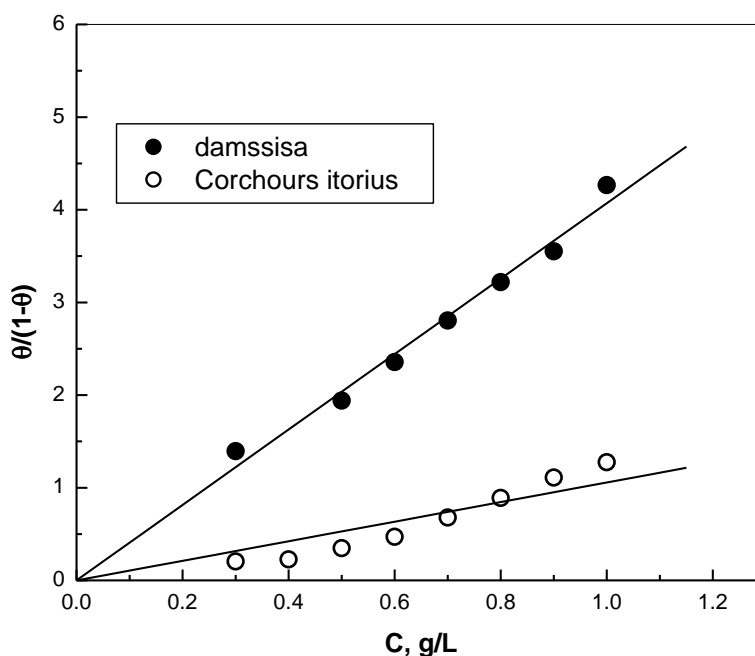


Figure 4. Linear fitting of the data of different extracts obtained from gasometry measurements to Langmuir isotherm.

And the kinetic - thermodynamic model is given by [27]

$$\text{Log} [\theta / (1 - \theta)] = \text{Log}K' + y\text{Log}C \tag{6}$$

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

$$K = K' (1/y) \tag{7}$$

Figures (4-6) show the application of the above mentioned models to the data of plants extract obtained from gasometry for aluminum surface. The parameters obtained from the figures are depicted in table 3.

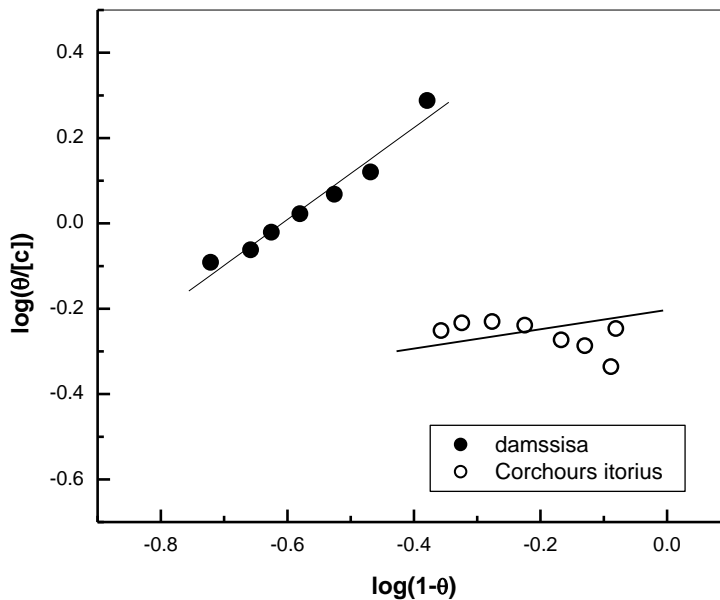


Figure 5. Linear fitting of the data of different extracts obtained from gasometry measurements to Flory Huggins isotherm.

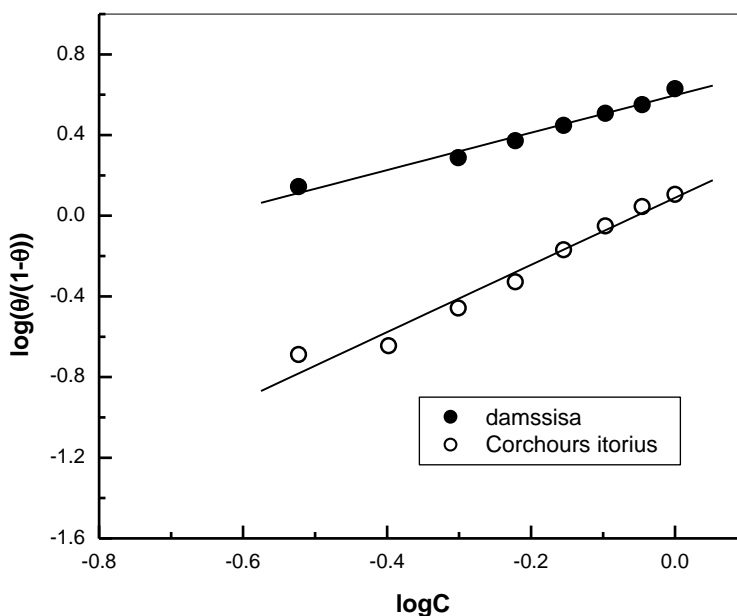


Figure 6. Linear fitting of the data of different extracts obtained from gasometry measurements to Kinetic-Thermodynamic model.

Table 3. Linear fitting parameters of Damsissa and Corchours itorius plants according to the used models

Extract	Model parameters				
	Langmuir	Flory-Huggins		Kinetic-Thermodynamic	
	K	K	x	K	1/y
Damsissa	4.07	4.20	1.1	4.41	1.1
Corchours itorius	1.06	1.32	0.6	1.16	0.5

It is clear that the Langmuir isotherm is applicable to fit the data of damsissa, and corchours itorius extract. On the other hand, the data of damsissa, and corchours itorius extract, the number of active sites occupied by a single inhibitor molecule, 1/y, were nearly equal to the size parameter x for the Damsissa and Corchours itorius extract. Since the efficiency of a given inhibitor was essentially a function of the magnitude of its binding constant K, large values of K indicate better and stronger interaction, whereas small values of K mean that the interaction between the inhibitor molecules and the metal is weaker. Hence, according to the numerical values of K obtained from Langmuir, Flory-Huggins or Kinetic-Thermodynamic model. The value of binding constant K is larger in the case of damsissa extract indicating that the extract of damsissa is more effective as corrosion inhibitor than corchours itorius.

3.2. Potentiodynamic polarization results

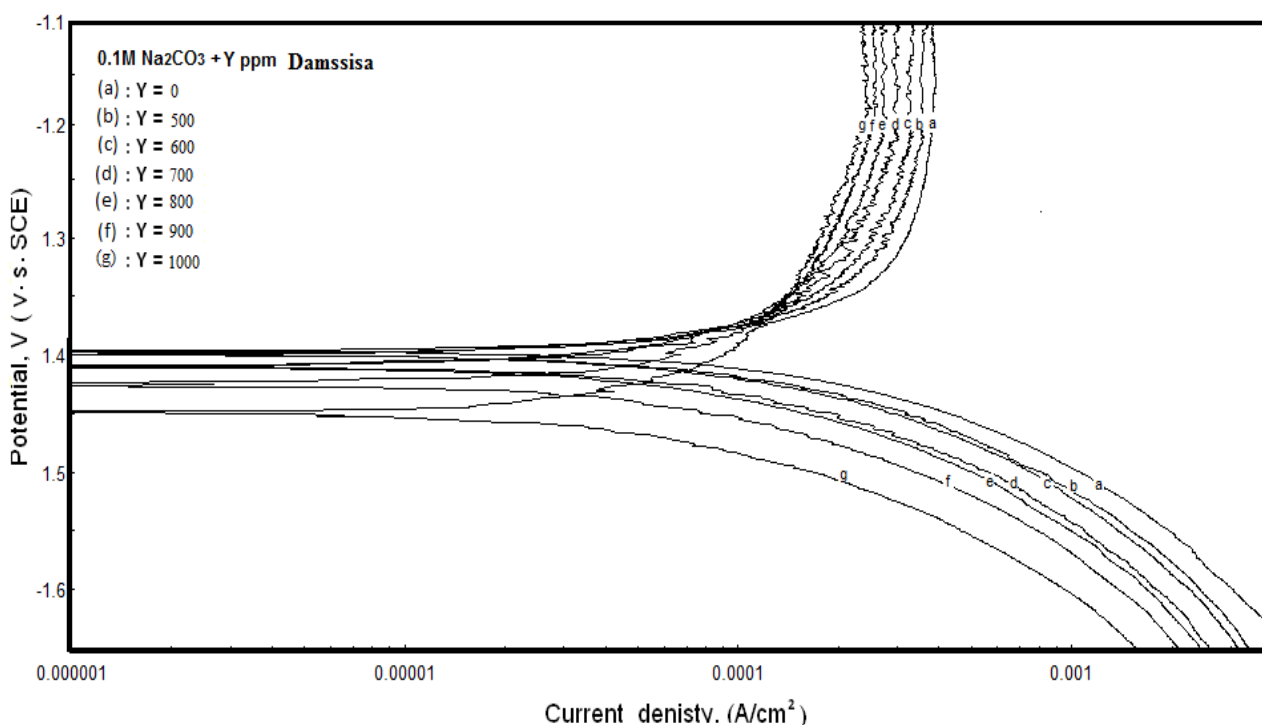


Figure 7. Potentiodynamic polarization curves for aluminum in 0.1 M sodium carbonate in absence and presence of different Damsissa extract concentrations.

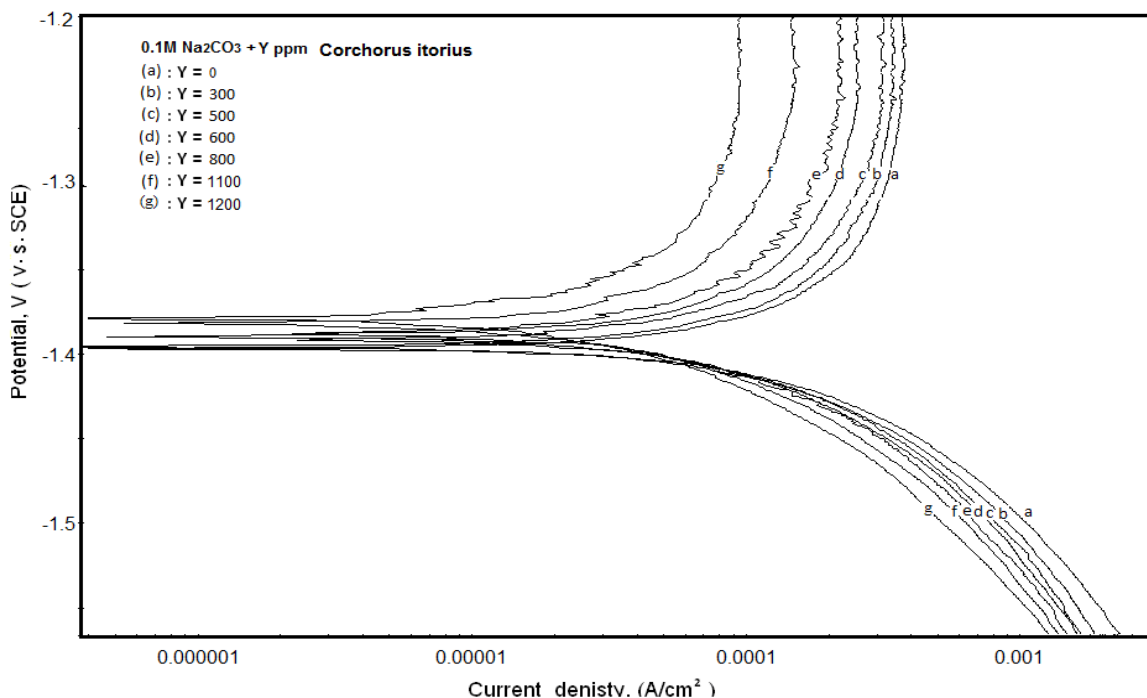


Figure 8. Potentiodynamic polarization curves for aluminum in 0.1 M sodium carbonate in absence and presence of different Corchours itorius extract concentrations.

Figures (7, 8) represent the anodic and cathodic polarization curves for aluminum in 0.1 M sodium carbonate in absence and presence of different plants extracts. As seen, from these figures the plant extracts inhibit both cathodic and anodic parts of the polarization curves; and the anodic polarization curves characterized by a limiting current, which indicates that the dissolution process of aluminum metal is mainly controlled by diffusion.

Table 4 shows the electrochemical polarization parameters, where the corrosion current density, (i_{corr}), was calculated from the intersection of anodic and cathodic Tafel lines; corrosion potential (E_{corr}); Corrosion current density and anodic and cathodic Tafel line slopes (β_a , and β_c) for different concentrations of Damsissa and Corchours itorius extract. The data revealed that, for all extracts under study, the corrosion current density that is directly proportional to corrosion rate decreases with increasing the Damsissa and Corchours itorius extract concentration. The values of E_{corr} for the two extractws shifted slightly to less negative potentials with increasing the concentration of extracts. The values of the anodic Tafel line slope (β_a) in presence of the extracts show higher values probably due to the effect of diffusion process.

The percentage of inhibition efficiency (% P) was calculated from the polarization measurements using the relation:

$$\% P = [(i_0 - i) / i_0] \times 100 \tag{8}$$

Where i_0 and i are the corrosion current density, in absence and presence of plants extracts. The tabulated data also indicate that Damsissa and Corchours itorius extracts inhibit the alkaline corrosion of aluminum efficiently and %P reaches about 90% for the solutions containing 1.0g/L of the extract.

Table 4. Electrochemical parameters for aluminum in 0.1 M sodium carbonate in absence and presence of different extracts concentrations.

Plant extract	Conc. (g/L)	$-E_{\text{corr}}$ (mV vs. SCE)	β_a (mV.decade ⁻¹)	β_c (mV.decade ⁻¹)	i_{corr} (mA.cm ⁻²)	% P
Damsissa	0.00	1462	111	184	0.38000	0.0
	0.05	1398	179	106	0.13941	63.3
	0.10	1396	164	99	0.12811	66.3
	0.20	1392	158	108	0.11982	68.5
	0.30	1394	142	94	0.09797	74.2
	0.40	1392	143	100	0.08968	76.4
	0.50	1395	134	92	0.08214	78.4
	0.60	1394	145	95	0.07310	80.8
	0.70	1399	123	100	0.06255	83.5
	0.80	1404	136	97	0.05803	84.7
	0.90	1418	105	86	0.04521	88.1
	1.00	1428	99	79	0.03466	90.9
	1.20	1444	88	84	0.03165	91.7
Corchours itorius	0.00	1462	111	184	0.38000	0.0
	0.05	1382	249	147	0.17784	53.2
	0.10	1386	229	132	0.17257	54.6
	0.20	1386	261	142	0.1477	61.1
	0.30	1389	234	123	0.13037	65.7
	0.40	1390	224	120	0.12283	67.7
	0.50	1387	253	128	0.11831	68.9
	0.60	1388	217	104	0.10249	73.1
	0.70	1384	216	111	0.09043	76.2
	0.80	1384	213	112	0.07988	78.9
	0.90	1385	239	106	0.06858	81.9
	1.00	1376	116	93	0.05501	85.5
	1.20	1380	206	99	0.04974	86.9
	1.50	1370	204	98	0.03542	90.7

In general, the cathodic reaction which occurs when Al corrodes in weakly alkaline solution has been investigated by Burstein and Liu.[28] using a guillotined electrode they proposed that the cathodic reaction is primarily the reduction of water to hydrogen according to



According to Drazic et al. [29], the corrosion of aluminum occurs through an oxide film via ionic migration through the oxide film followed by dissolution at the oxide/electrolyte interface. The overall anodic reaction in the corrosion of Al in weakly alkaline solutions is:



Since there is always an oxide or hydroxide film on the electrode surface, the current for the anodic reaction does not increase exponentially as the potential is made more anodic as is found [30]. There are two possibilities for the slow step:

1. $\text{Al}(\text{OH})_3$ and OH^- are in equilibrium with $\text{Al}(\text{OH})_4^-$ at the aqueous solution/oxide (or hydroxide) interface and the slow step is the mass transfer of $\text{Al}(\text{OH})_4^-$ from the surface into the bulk of the solution.

2. OH^- is in equilibrium between the aqueous solution/oxide/hydroxide interface and the slow step is the formation of $\text{Al}(\text{OH})_4^-$.

These two possibilities can readily be distinguished, since a change in the diffusion layer thickness at the electrode will cause the anodic current to increase only in case 1, which occur in our case. The earliest studies [31-33] have been suggested a similar mechanism considered that the slow step in the anodic dissolution of aluminum in alkaline solution is diffusion of AlO_2^- anion from the metal surface to the bulk of solution.

3.3. Electrochemical impedance spectroscopy results

Figures (9,10) show the Nyquist impedance plots for aluminum in 0.1 M Na_2CO_3 in the absence and presence of different concentrations of Damsissa and Corchours itorius extracts. The Nyquist impedance plots explain that the impedance response consists of capacitive semicircle followed by inductive loop indicating that the dissolution process occurs under activation control. The inductive loop is generally attributed to the adsorption of the species resulting from metal dissolution and hydrogen adsorption [34]. The impedance spectra for different Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit model (figure 11) which includes the solution resistance R_s and the double layer capacitance (Q_{dl}) which is placed in parallel to charge transfer resistance element, R_{ct} . The R_{ct} value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate. The electrochemical impedance parameters obtained from the analysis of experimental data are given in table 5.

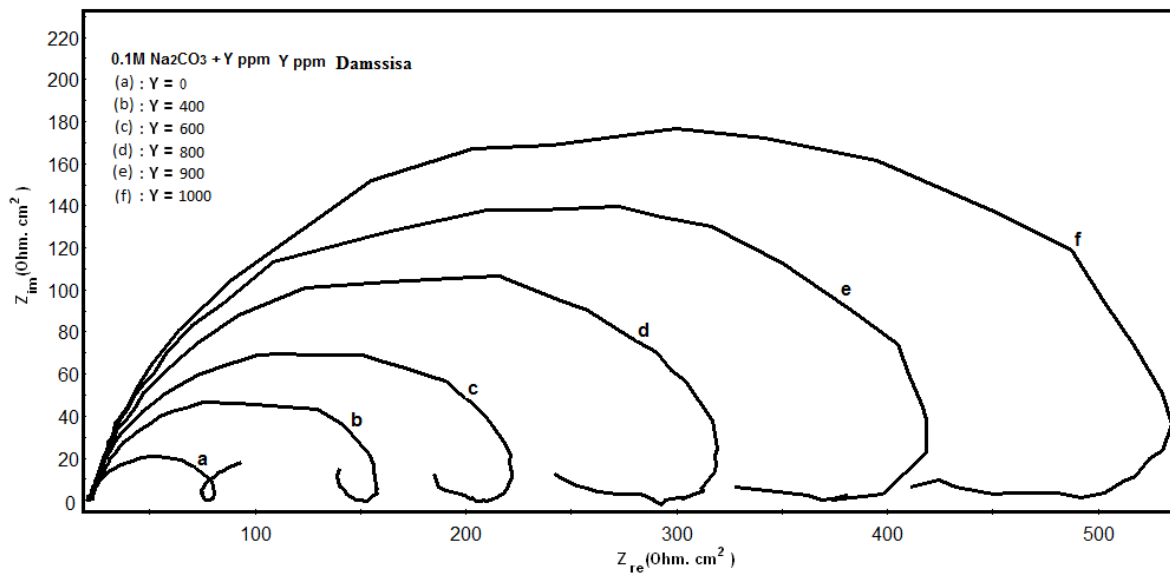


Figure 9. Nyquist plots for aluminum in 0.1 M sodium carbonate in absence and presence of different Damssisa extract concentrations.

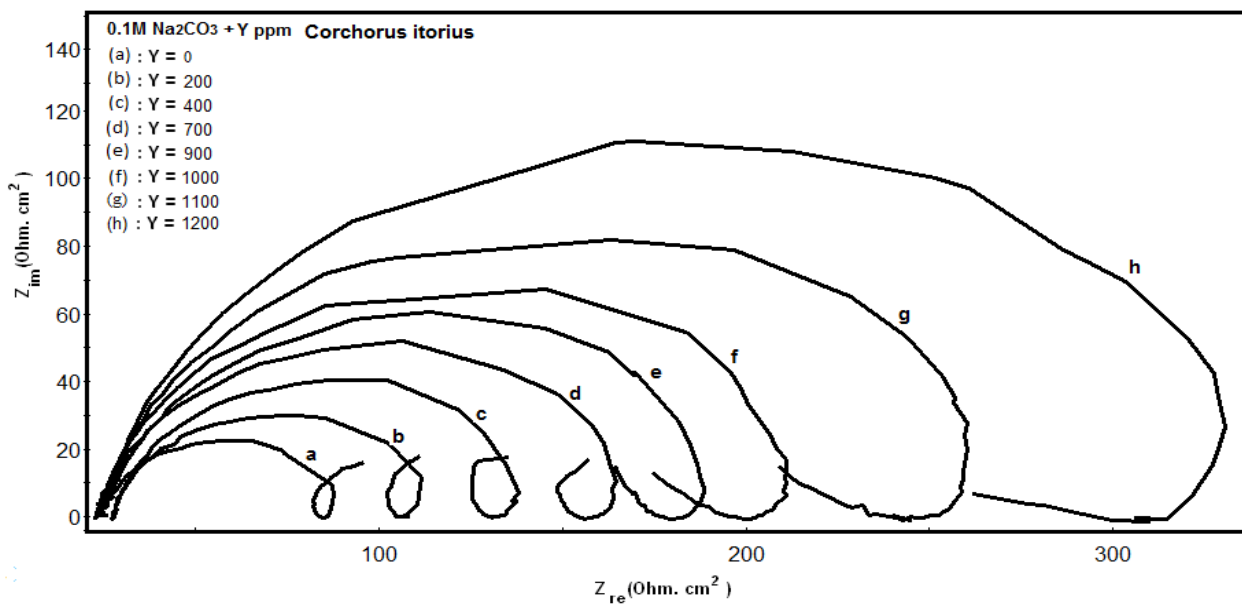


Figure 10. Nyquist plots for aluminum in 0.1 M sodium carbonate in absence and presence of different Corchorus itorius extract concentrations.

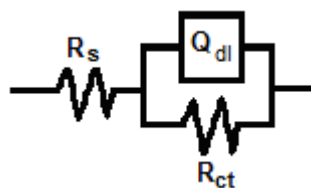


Figure 11. The equivalent circuit model.

Table 5. Electrochemical impedance parameters of aluminum 0.1M sodium carbon containing different extracts concentration.

Plant extract	Conc. (g/L)	R_s (Ohm.cm ²)	Q (μF.cm ⁻¹)	n	R_{ct} (Ohm.cm ²)	% P
Damsissa	0.00	21.8	26.6	0.9	58.5	0.0
	0.10	25.9	23.9	0.9	60.5	3.3
	0.20	23.4	20.7	0.9	84.2	30.5
	0.30	24.0	21.7	0.9	110.2	46.9
	0.40	22.7	22.7	0.9	129.7	54.8
	0.50	22.9	24.0	0.9	143.4	59.2
	0.60	21.9	22.7	0.9	194.3	69.8
	0.70	23.7	20.7	0.9	256.8	77.2
	0.80	22.8	22.6	0.9	281.6	79.2
	0.90	22.2	24.6	0.9	488.7	88.0
	1.00	22.3	26.2	0.9	593.5	90.1

Corchours itorius	0.00	21.8	26.6	0.9	58.5	0.0
	0.10	26.2	19.7	0.9	65.7	10.9
	0.20	28.2	23.5	0.9	80.3	27.1
	0.30	27.6	22.9	0.9	88.5	33.9
	0.40	28.2	21.1	0.9	105.2	44.4
	0.50	26.3	19.8	0.9	120.1	51.3
	0.60	25.9	22.1	0.9	129.8	54.9
	0.70	24.7	21.4	0.9	134.3	56.4
	0.80	25.3	23.3	0.9	168.2	65.2
	0.90	22.2	24.0	0.9	220.4	73.5
	1.00	26.6	22.5	0.9	296.3	80.3
	1.20	25.7	21.2	0.9	399.3	85.2
	1.50	24.8	20.5	0.9	533.4	89.1

Increasing R_{ct} values with the concentration of the extract, for all extracts under study, suggesting decrease of the corrosion rate since the R_{ct} value, is a measure of electron transfer across the surface, and inversely proportional to the corrosion rate. The decrease in the Q_{dl} values could be attributed to the adsorption of the chemical constituents of the extracts at the metal surface [35]. The

percentage of inhibition efficiency (% P) was calculated from the impedance measurements using the relation:

$$\% P = [(R_{ct} - R_{cto}) / R_{ct}] \times 100 \tag{11}$$

Where R_{ct} and R_{cto} are the charge transfer resistance, in presence and absence of Damsissa and Corchours itorius extract respectively. The tabulated data also indicate that Damsiss and Corchours itorius extract has considerable effect for the corrosion of aluminum in 0.1 M Na_2CO_3 solution .

As seen, the inhibition efficiency for 1g/L of the extracts is arranged according to table 6. The data show that: there is a considerable agreement between the data obtained from the two techniques and damsissa extract is more effective than the Corchours itorius extract in inhibition of the corrosion of aluminum in 0.1 M Na_2CO_3 solution .

Table 6. comparison between %P of Damsissa and Corchours itorius extracts (1g/L) which obtained from polarization and impedance technique.

Type of plant	%P	
	Polarization	Impedance
Damsissa	90.9	90.1
Corchours itorius	85.5	80.1

3.4. Mechanism of corrosion of aluminum in alkaline solutions

a) The anodic reaction (dissolution of aluminum):

The anodic potintiodynamic polarization curves of aluminum in 0.1M Na_2CO_3 in absence or in presence of the extracts show a limiting current indicating that the dissolution of aluminum is controlled by the diffusion of $Al(OH)_4^-$ or AlO_2^- from the surface of the metal to the bulk of solution. Then the anodic dissolution of aluminum can be represented as :



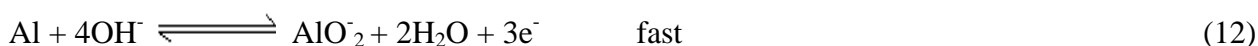
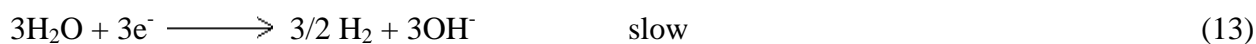
b) The cathodic reaction (reduction of water):

The cathodic polarization curve of aluminum in 0.1M Na_2CO_3 in absence or in presence of the extracts show Tafel behaviour indicating that the reduction process is controlled by charge transfer and can be presented by



c) *The overall corrosion reaction:*

The impedance spectroscopy data of aluminum 0.1M Na₂CO₃ in absence or in presence of the extracts measured at the equilibrium potential indicated that the corrosion of aluminum is controlled by charge transfer. This means that the reduction of water at cathodic areas is the slow step of corrosion of aluminum. The equation corresponding to the overall reaction of corrosion of aluminum in in 0.1M Na₂CO₃ solution can be obtained if equation (9) is multiplied by 3 and then added to equation (12):



4. CONCLUSIONS

1. Extracts of Damssisa and Corchours itorius act as mixed type inhibitors for the alkaline corrosion of aluminum.
2. The anodic dissolution of aluminum is controlled by diffusion of AlO₂⁻ ion from the surface of the metal to bulk solution.
3. Impedance results obtained at the equilibrium potential of aluminum in 0.1M Na₂CO₃ solutions indicated that the rate determining step of the overall alkaline corrosion reaction of aluminum is controlled by the charge transfer process of the reduction of water at cathodic areas.
4. A mechanism of the corrosion of aluminum metal in 0.1M Na₂CO₃ was proposed.

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