
CORROSION INHIBITION OF AL-CU ALLOY IN ACIDIC MEDIA BY CASSIA ACUTIFOLIA EXTRACT.

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Abstract

The inhibitive action of aqueous extract of Cassia acutifolia (CA) plant on Al-Cu alloy corrosion in 2M HCl, H₃PO₄ and H₂SO₄ solutions was studied using weight loss, potentiodynamic and impedance measurements. The inhibition was found to increase with increasing concentration of CA extract. The adsorption behaviour of CA extract followed Flory – Huggins and thermodynamic – Kinetic isotherms. The effect of temperature range (25-65°C) on the corrosion behaviour of Al-Cu alloy in 2M HCl solution indicated that the inhibition efficiency of CA extract decreases with rise of the temperature leading to physical adsorption. Thermodynamic parameters are calculated from Arrhenius transition state equation. Polarization curves showed that CA extract acts as cathodic type inhibitor. Tafel slopes are more or less constant suggesting that the action of CA extract does not affect the mechanism of corrosion process. The results obtained show that the CA extract could serve as an effective inhibitor for the corrosion of Al-Cu alloy in HCl solution.

Keywords: Corrosion inhibition, Natural extract, Al alloy.**Introduction:**

The protection of metals or alloys against corrosion can be achieved either by special treatment of the medium to depress its aggressiveness by introducing in small amounts of special substances called corrosion inhibitors⁽¹⁾. Most of reserches were devoted to study the corrosion inhibition of metals and alloys in aqueous media using large number of organic compounds⁽²⁻¹⁰⁾, which may be very expensive and toxic to both human and environment. Recently started to study the application of natural products of some common plant extracts as corrosion inhibitors which are ecofriendly and harmless. Few of natural products⁽¹¹⁻¹⁴⁾ were previously used as corrosion inhibitors for aluminium and its alloys in acidic media.

There is no reports in the literature on the use of Cassia acutifolia (CA), therefore the aim of the present work is to elucidate the effect of the plant extract of CA as corrosion inhibitor for Al-Cu alloy in acidic media, using chemical and electrochemical techniques.

Experimental:

Materials and electrolytes:

Corrosion tests were performed on Al-Cu alloy, of chemical composition (w%): 94.750 Al, 3.980 Cu, 0.725 Fe and 0.550 Mn using EDAX. Al alloy sheets with dimension of 3.0 x 1.0 x 0.2 cm were used for weight loss measurements. For polarization and impedance measurements, a cylindrical rod mounted into glass tube by epoxy resin, with surface area of 1.68 cm². Before each experiment, the electrode surface was mechanically polished using successive grades of emery papers down to 4/0, and degreased with ethanol and then washed several times with bidistilled water and dried. The electrolytic solutions HCl, H₃PO₄ and H₂SO₄ were prepared using Analar grade reagents, and bidistilled water. Preparation of plant extract, CA Fig.(1) is carried out by boiling weighed amounts of powder of the crused seeds of plant. After filtration, the liquid was evaporated in an oven at 50°C for 48 hours. Crystalline precipitate is formed. The concentrations are expressed as w/v.

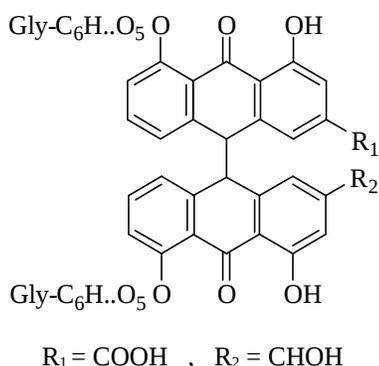


Fig.(1) The main chemical component in *Cassia acutifolia* (Sennoside)⁽¹⁵⁾

Weight loss measurements:

Weight loss measurement was recorded by the usual procedure⁽¹⁶⁾ at temperature range 25-65°C with and without of different concentrations of plant extract. Triplicate samples were used to check reproducibility of results. Corrosion rates were expressed in g/cm².min , and the percentage inhibition efficiency⁽¹⁷⁾ (IE%) was calculated from the following relationship :

$$IE\% = \left[1 - \left(\frac{R_{inh}}{R_{free}} \right) \right] \times 100$$

(1)

Where R_{free} and R_{inh} are corrosion rate of alloy sheet in free and inhibited solutions, respectively.

Electrochemical Measurements:

The potentiodynamic polarization (PDP) and the electrochemical impedance spectroscopy (EIS) are carried out in a conventional three-compartment cell with a cylindrical rod of Al-Cu alloy as working electrode. A saturated calomel electrode (SCE) used as reference and Platinum wire as counter electrode.

PDP and EIS measurement were achieved using ACM Gill AC connected to a Samsung computer. The frequency range for EIS of 100 kHz – 10 mHz with applied signal amplitude of 30mV around the rest potential. Before the measurements the working electrode was introduced into the test solution and left for 10 min at open circuit potential. Polarization curves were obtained at scan rate of 5 mV/min starting from cathodic potential going to anodic direction. All the measurements were done at $25 \pm 1^\circ\text{C}$ in aerated solutions and under unstirred conditions.

Results and discussion:

Weight loss measurements:

Al-Cu samples were immersed in aerated solutions of HCl, H_3PO_4 and H_2SO_4 of different concentrations range (0.5- 2.5 M) along a period of 60 min, Table (1) shows the variation of calculated corrosion rate (R_{corr}) with the concentration of the acid. It is indicated from the results that the corrosion rate is decreased in the order :



Table (1): Corrosion of Al-Cu alloy in different concentrations of acidic media.

Concentration (M)	HCl	H_3PO_4	H_2SO_4
	Corrosion rate ($\text{g}/\text{cm}^2.\text{min.}$)		
0.5	3.77e-5	5.47e-6	1.69e-6
1.0	1.81e-4	6.07e-6	2.13e-6
1.5	5.34e-4	7.24e-6	2.89e-6
2.0	1.39e-3	8.20e-6	3.64e-6
2.5	2.32e-3	9.93e-6	4.50e-6

Fig.2 (a,b,c) represents the relation between weight loss (g/cm^2) and the immersion time for Al-Cu alloy in 2.0 M of HCl, H_3PO_4 , and H_2SO_4 solutions in absence and presence of different concentrations (0.4 to 8.0 g/L) of *Cassia acutifolia*, CA. As can be seen from the curves, there is a remarkable decrease in weight loss comparing with blank solutions signified corrosion inhibition. The linearity with time indicates that the absence of insoluble surface film during corrosion, and the inhibitor was adsorbed onto the metal surface and thereafter, inhibits the corrosion process⁽¹⁸⁾

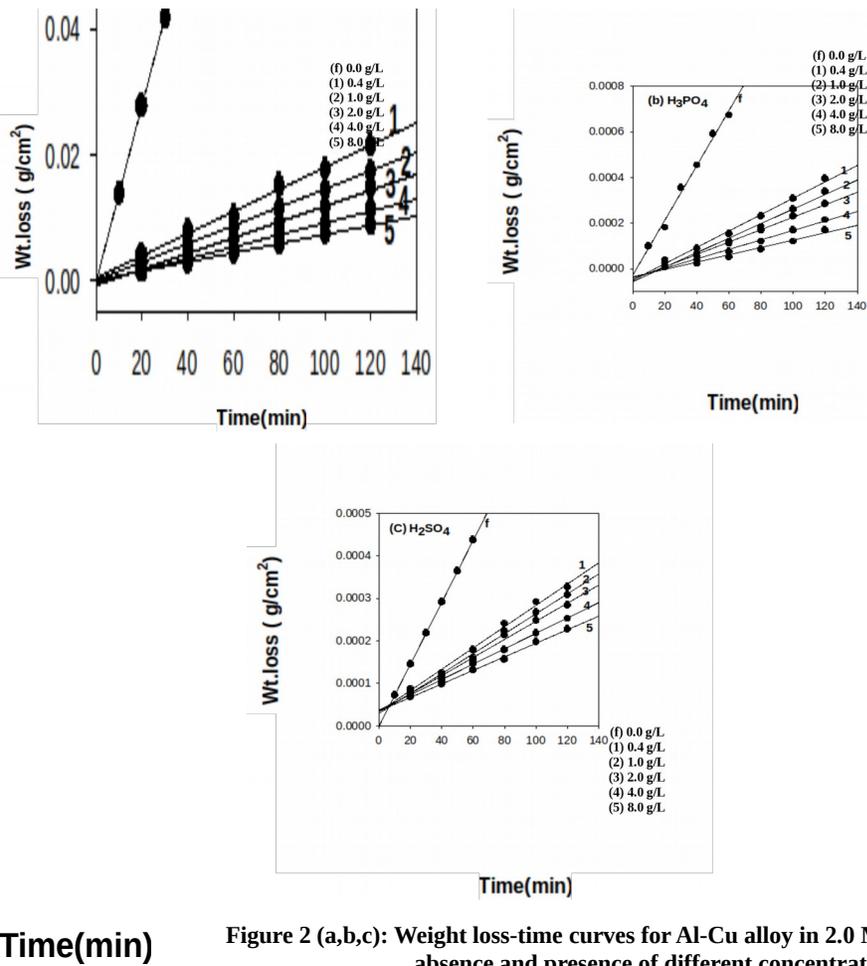


Figure 2 (a,b,c): Weight loss-time curves for Al-Cu alloy in 2.0 M acidic media in absence and presence of different concentrations of CA extract at 25°C.

The degree of the surface coverage Θ which represents the part of the metal surface covered by inhibitors molecules was calculated using the following equation⁽¹⁶⁾.

$$\theta = 1 - \left(\frac{R_{inh}}{R_{free}} \right) \quad (2)$$

The values of R_{corr} , IE% and Θ at different concentrations of CA extract in 2.0M acidic media are listed in Table (2). Inspection of this Table, revealed that as CA extract concentration is increased, R_{corr} decreases while the IE% and Θ increase. The increase of Θ may be due to the increase of the number of adsorbed molecules of CA extract on Al-Cu alloy surface. A good inhibition efficiency percent observed at 8.0 g/L, with 94.66% in 2.0 M HCl solution.

Table (2): Effect of CA extract concentration on R_{corr} , IE% and Θ for Al-Cu alloy in 2.0M acidic media at 25°C.

C_{inh} (g/L)	HCl			H_3PO_4			H_2SO_4		
	R_{corr}	%IE	Θ	R_{corr}	%IE	Θ	R_{corr}	%IE	Θ
0.4	1.74e-4	87.48	0.875	3.59e-6	56.22	0.562	2.51e-6	31.04	0.310
1.0	1.45e-4	89.57	0.896	3.16e-6	61.46	0.615	2.35e-6	35.44	0.354
2.0	1.25e-4	91.01	0.910	2.72e-6	66.83	0.668	2.14e-6	41.21	0.412
4.0	9.63e-5	93.07	0.931	2.06e-6	74.88	0.749	1.81e-6	50.27	0.503
8.0	7.42e-5	94.66	0.947	1.62e-6	80.24	0.802	1.59e-6	56.32	0.563

Adsorption isotherm:

The adsorption of organic adsorbate on the surface of metal is regarded as substitutional adsorption process between the organic compound in the aqueous phase (Org_{aq}) and the water molecules adsorbed on the metal surface ($(H_2O)_{ads}$)⁽¹⁹⁾.



Where x is the number of water molecules replaced by one organic molecule. The variation of surface coverage Θ with concentration of CA extract in acidic media is shown in Fig.(3).

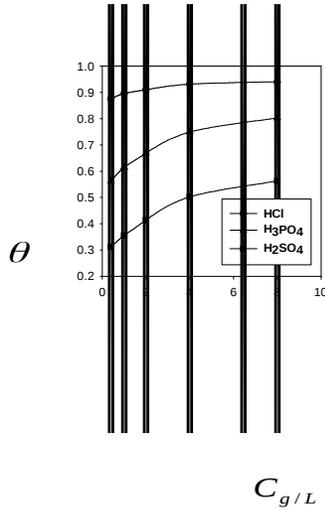


Fig. (3) :Variation in surface coverage with concentration of CA extract in 2.0 M acidic .media at 25°C

To clarify the nature of adsorption of CA extract on the Al-Cu alloy surface, the theoretical fitting of Flory- Huggins and the kinetic thermodynamic models were investigated in 2M HCl, H_3PO_4 and H_2SO_4 solutions.

Flory – Huggins isotherm is given by⁽²⁰⁾

$$\theta / [x(1 - \theta)^x] = K[C] \quad (4)$$

where x is the number of adsorbed water molecules substituted by a given inhibitor molecule.

The kinetic – thermodynamic model is given by⁽²¹⁾

$$\log[\theta/(1 - \theta)] = \log k + y \log C \quad (5)$$

where y is the number of inhibitor molecules occupying one active site. Value of $y > 1$ imply the formation of multilayer of inhibitor molecules on the metal surface, and when $y < 1$ indicate that the given inhibitor will occupy more than one active site. The binding constant K is given from the intercept of equation(5).

The relation between the binding constant of the adsorption (K) and the standard free energy of adsorption ΔG_{ads}^o is given by the following equation:

$$K = \left(\frac{1}{C_{H_2O}} \right) \exp \left(\frac{- \Delta G_{ads}^{\circ}}{RT} \right) \quad (6)$$

Where C_{H_2O} is the concentration of water molecules (g/L) at electrode/electrolyte interface at 25°C, R is the gas constant (8.314 J/mol/degree) and T is the absolute temperature. Figs. (4,5) show the linear fitting of CA extract in acidic media according to the isotherm models.

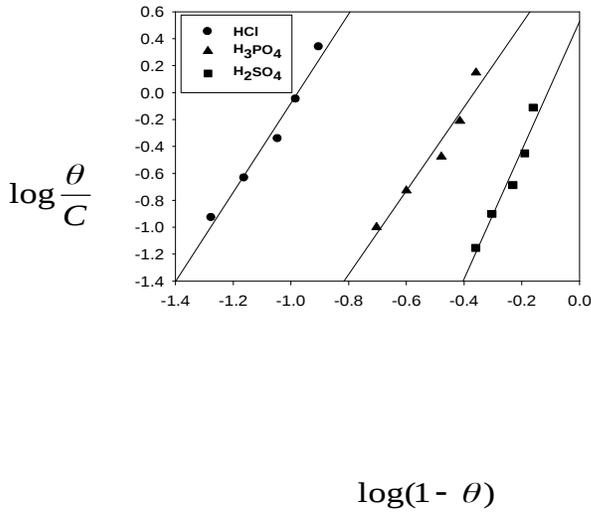
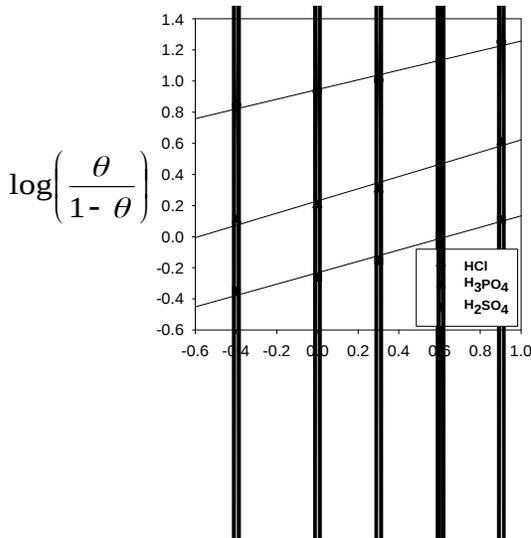


Fig. (4) :Linear fitting of CA extract for Al-Cu alloy in 2.0 M acidic media to Flory-Huggins isotherm at 25°C.



$$\log C$$

Fig. (5) :Linear fitting of CA extract for Al-Cu alloy in 2.0 M acidic media .to kinetic-thermodynamic isotherm at 25°C

The parameters of K , y , $1/y$, x and ΔG_{ads}° are given in Table (3). It is clear that the values of x , $1/y$ indicate that, more than one water molecule displacing from the surface, and CA molecules will occupy more than one active site , K values is large in HCl solution. This means that the stronger interaction between CA extract and Al-Cu alloy surface takes place in HCl solution. The calculated values of ΔG_{ads}° are low suggesting that the nature of the inhibitor adsorption is mainly physical adsorption and negative sign meaning spontaneous interaction of inhibitor molecule with corroding metal surface⁽²²⁾. According to the values of K , the inhibition efficiency of CA extract in acidic media could be arranged in the order :



Table (3) : Linear fitting parameters and the standerd free energy of CA extract for Al-Cu alloy in 2.0M acidic media at 25°C .

Acids (M)	Kinetic-thermodynamic				Flory-Huggins		
	Y	1/Y	K (g ⁻¹ l)	$-\Delta G_{ads}^{\circ}$ (kJ/ g ⁻¹ L)	X	K (g ⁻¹ l)	$-\Delta G_{ads}^{\circ}$ (kJ/g ⁻¹ L)
HCl	0.31	3.23	1132.31	34.54	3.31	516.50	32.60
H ₃ PO ₄	0.39	2.56	3.85	20.46	3.10	4.3700	20.77
H ₂ SO ₄	0.37	2.70	0.24	13.58	4.77	0.7100	16.27

Activation energy calculation:

The effect of temperature range (25-65°C) on R_{corr} and IE% of Al-Cu alloy in 2.0M HCl, H₃PO₄ and H₂SO₄ solutions in absence and presence of 4.0 g/L of CA extract, using weight loss method. Table (4) indicate that R_{corr} in absence and presence of CA extract increased with rise in temperature, indicating that CA extract was adsorbed on alloy surface at all temperatures. Also IE% decreases with

increasing temperature, and the high IE% at 25°C. These suggests a physical adsorption of CA extract on Al-Cu alloy surface.

Table (4): Effect of temperatures on R_{corr} and IE% for Al-Cu alloy in 2.0M acidic media in absence and presence 4.0 g/L of CA extract.

	HCl			H ₃ PO ₄			H ₂ SO ₄		
	R_{corr} g/cm ² .min		IE%	R_{corr} g/cm ² .min		IE%	R_{corr} g/cm ² .min		IE%
$C_{inh.}(g/L)$	0.0	4.0	4.0	0.0	4.0	4.0	0.0	4.0	4.0
25 °C	1.39e-3	9.63e-5	93.07	8.20e-6	2.06e-6	74.88	3.64e-6	1.81e-6	50.27
35 °C	2.85e-3	3.99e-4	86.00	1.55e-5	4.98e-6	67.87	6.33e-6	3.44e-6	45.66
45 °C	4.70e-3	1.01e-3	78.51	2.00e-5	9.45e-6	52.75	8.00e-6	5.24e-6	34.50
55 °C	6.82e-3	2.56e-3	62.46	3.00e-5	1.85e-5	38.33	1.11e-5	8.34e-6	24.86
65 °C	8.73e-3	4.50e-3	48.45	3.80e-5	2.63e-5	30.79	1.55e-5	1.26e-5	18.71

Arrhenius plot for R_{corr} (g cm⁻² min⁻¹) vs $1/T$ (°K⁻¹) is found to be linear Fig.6(a,b) . The energy of activation (E_a^*) is calculated from the slope of this plot.

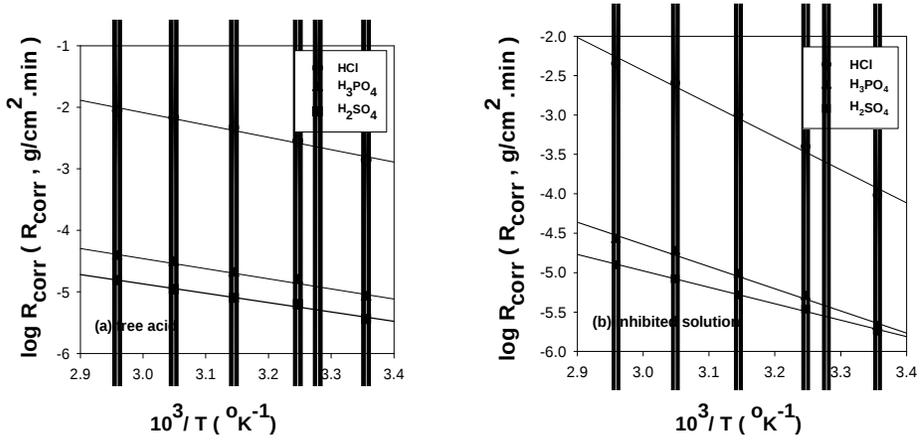


Fig.6(a,b) :Arrhenius plots of the corrosion rate for Al-Cu alloy in 2.0 M acidic media in absence and presence of CA extract

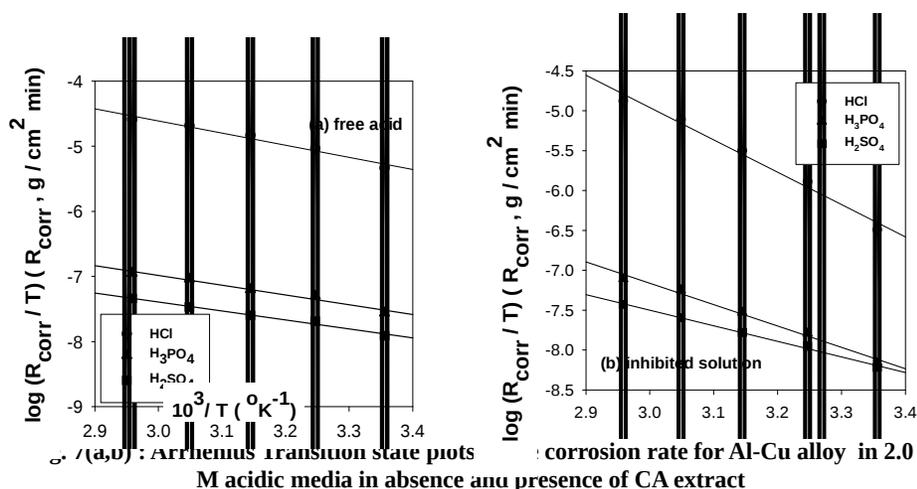
Activation thermodynamic parameters of Al-Cu alloy in acidic media in absence and presence of CA extract is given by Arrhenius transition state equation⁽²³⁾.

$$R_{corr} = \left[\left(\frac{RT}{Nh} \right) \exp \left(\frac{\Delta S^*}{R} \right) \right] \exp \left(\frac{-\Delta H^*}{RT} \right) \quad (7)$$

where h is plank's constant, N is Avogadro's number and ΔS^* , ΔH^* are the activation entropy and enthalpy, respectively. A plot of $\log \frac{R_{corr}}{T}$ vs $\frac{1}{T}$ gives

straight line with slope of $\left[\frac{-\Delta H^*}{2.303R} \right]$ and an intercept of

$$\left[\log \left(\frac{R}{Nh} \right) + \left(\frac{\Delta S^*}{2.303R} \right) \right], \text{ represented in Fig.7(a,b) .}$$



The calculated values of activation parameters E_a^* , ΔH^* and ΔS^* in the absence and presence of different CA extract are shown in Table (5). It is clear that, E_a^* increases in the presence CA extract, suggested that the corrosion inhibition of CA occurred through physical adsorption. Also higher ΔH^* values indicate that, the degree of surface coverage decreased with rise in temperature, supporting the proposed physical adsorption mechanism. The entropy ΔS^* in absence and presence of CA extract is large and negative meaning that the increasing in ordering accompanied the dissolution process.

Table (5): The values of activation parameters E_a^* , ΔH^* and ΔS^* for Al-Cu alloy in 2.0 M acidic media in the absence and presence of CA extract.

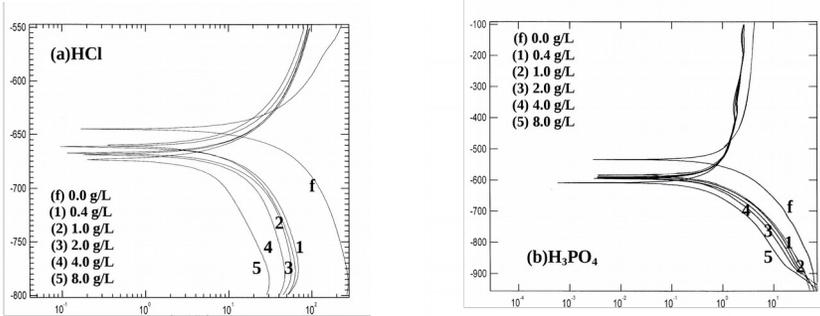
Acids (M)	free acids			Inhibited solution		
	E_a^* kJ/mol	ΔH^* kJ/mol	ΔS^* J/°K/mol	E_a^* kJ/mol	ΔH^* kJ/mol	ΔS^* J/°K/mol
HCl	38.34	35.71	178.77-	80.36	77.72	59.38-
H_3PO_4	31.37	28.73	245.10-	53.89	51.25	181.00-
H_2SO_4	29.05	26.41	259.93-	40.00	37.37	229.11-

Polarization measurements:

Fig.8(a,b,c) collects the anodic and cathodic curves of Al-Cu alloy in aerated 2.0M HCl, H₃PO₄ and H₂SO₄ solutions in absence and presence of different concentrations (0.4 – 8.0 g/L) of CA extract. The curves produces a little shift on the anodic region and a greater shift on the cathodic region. The anodic and cathodic reactions⁽¹⁾ involved the corrosion of metal in acidic solutions are



The adsorbed inhibitor blocks either the anodic or cathodic reaction or both. The effect of the inhibitor may be due to changes in the electric double layer, by reducing metal reactivity, or by the inhibitor participation in partial electrode reaction and by formation of a physical barrier. The adsorbed inhibitor occupies sites which are electrochemically active and thereby reduces the extent of anodic or cathodic reaction or both.



Current (mA/cm⁻²)

Fig.8(a,b,c) :Potentiodynamic polarization curves for Al-Cu alloy in 2.0 M acidic media in absence and presence of different CA extract concentrations at 25°C.

The electrochemical parameters E_{corr} , i_{corr} , B_a , B_c and IE% are given in Table(6). The inhibition efficiencies are defined as :

$$IE\% = 100 \times \left(1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^o} \right) \quad (11)$$

where i_{corr} , i_{corr}^o refer to corrosion current densities of inhibited and uninhibited acidic media, determined by extrapolation of Tafel lines to corrosion potential. Inspection of the Table reveals that E_{corr} shifted towards the cathodic direction. This suggested that in acidic medium the inhibition is due to the adsorption of the inhibitor on an oxide-free metal surface and prevention of hydrogen evolution reaction at the cathodic sites. The step involves displacement of pre-adsorbed water molecules by the inhibitor followed by electrochemical reaction at the surface. The inhibitor which restrict the diffusion to the alloy surface and thus block the cathodic reduction of oxygen are called cathodic inhibitor and help to form thick surface layer.



The values of the corrosion current densities i_{corr} decreases with increasing the concentration of CA extract, indicating that the inhibitive property of the plant extract is concentration dependent. Tafel slopes B_a , B_b are more or less constant suggesting that the inhibiting action of CA extract does not affect the mechanism of the corrosion process. Also IE% in acidic media increases with their concentration, and at 8.0 g/L it gives the high efficiency 93.10% in 2.0M HCl solution at 25°C..

. Table (6): Potentiodynamic parameters of Al-Cu alloy in 2.0 M acidic media with different concentrations of CA extract at 25°C

C_{inh} (g/l)	HCl					H_3PO_4					H_2SO_4				
	E_{corr} - mV	i_{corr} mA/cm ²	β_a mV/dec	β_c mV/dec	$\Delta E\%$	E_{corr} . mV	i_{corr} mA/cm ²	β_a mV/dec	β_c mV/dec	$\Delta E\%$	$-E_{corr}$. mV	i_{corr} mA/c m ²	β_a mV/dec	β_c mV/dec	$\Delta E\%$
0.0	645.0	75.76	65.52	70.32	-	535.6	2.96	130.9	99.95	-	532.7	1.46	115.2	67.63	-
0.4	661.4	11.45	58.37	67.05	84.89	583.4	1.25	129.0	89.74	57.77	553.2	1.01	112.0	64.81	30.82
1.0	660.0	9.63	53.12	66.91	87.29	592.0	1.12	127.1	86.89	62.16	565.6	0.96	109.3	63.92	34.25
2.0	669.5	8.10	51.62	64.23	89.31	593.7	0.92	122.7	91.97	68.92	573.3	0.85	110.8	62.75	41.78
4.0	670.7	6.80	50.62	60.23	91.02	597.1	0.82	125.8	88.81	72.30	582.5	0.71	111.0	66.13	51.37
8.0	674.2	5.23	48.79	56.94	93.10	609.1	0.60	124.0	92.13	79.73	596.5	0.62	110.3	64.61	57.53

Electrochemical impedance spectroscopy (EIS):

The Fig.9(a,b,c) shows the Nyquist plots for Al-Cu alloy in acidic media in absence and presence of various concentrations of CA extract at 25°C.

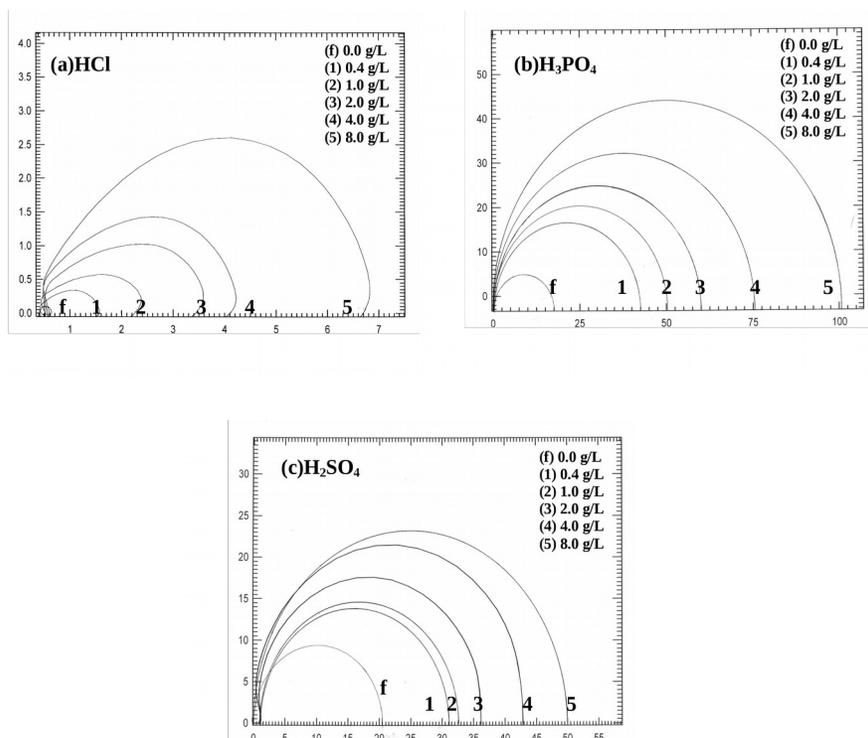


Fig. 9. Nyquist plots of Al-Cu alloy in (a) HCl, (b) H₃PO₄, and (c) H₂SO₄ acidic media in absence and presence of different CA extract concentrations at 25°C

The presence of inhibitor led to change of the impedance plots in both shape and size. The plots exhibited depressed semicircles with center below the real axis. This phenomenon could be related to the surface heterogeneity due to the microscopic roughness of the electrode surface and distribution of active sites adsorption of inhibitor⁽²⁴⁾. Also the size of the capacitive loops are increased by increasing the concentration of CA extract. This indicated that CA increased the charge transfer resistance and then it had an inhibiting effect on Al-Cu alloy in acid electrolyte solution. The inhibition efficiencies had the same trend of those obtained from the weight loss and potentiodynamic measurements. The inhibition efficiency IE% is calculated from the charge transfer R_{ct} , using the following equation :

$$IE\% = \left[1 - \left(\frac{R_{ct_{inh}}}{R_{ct_{corr}}} \right) \right] \times 100 \quad (13)$$

Table (7) shows that by increasing the CA extract concentration the charge transfer resistance, R_{ct} and IE% values increased. The higher R_{ct} , the lower corrosion rate and more efficient is the inhibitor.

Based upon the experimental results, the inhibition effect of CA extract can be related to an physical adsorption process, it contains of organic compounds e.g. anthraquinone, glucoside flavonoid and alkaloid, these containing electrophilic substituents as N_2 and O_2 which decrease the electron density at an adsorption centers of plant extract molecules and facilitate the adsorption of molecules on a negatively charged sites and reduce corrosion.

Table (7): Impedance parameters of Al-Cu alloy in 2.0 M acidic media with different concentrations of CA extract at 25°C

C_{inh} (g/L)	HCl			H_3PO_4			H_2SO_4		
	C_{dl} $\mu F /$ (cm^2)	R_{ct} $\Omega .$ (cm^2)	IE%	C_{dl} $\mu F /$ (cm^2)	R_{ct} $\Omega .$ (cm^2)	IE%	C_{dl} $\mu F /$ (cm^2)	R_{ct} $\Omega .$ (cm^2)	IE%
0.0	1.29e-2	0.194	-	1.33e-3	16.96	-	9.18e-4	20.56	-
0.4	1.20e-2	1.42	86.34	1.17e-3	42.94	60.50	4.00e-4	30.94	33.55
1.0	1.18e-2	2.00	90.30	9.48e-4	49.22	65.54	3.78e-4	32.44	36.62
2.0	2.44e-3	2.54	92.36	6.30e-4	58.31	70.91	3.74e-4	36.31	43.38
4.0	9.67e-4	3.35	94.21	4.22e-4	72.42	76.58	2.69e-4	41.99	51.04
8.0	4.81e-4	6.45	96.99	2.91e-4	94.14	81.98	2.19e-4	49.55	58.51

Also attractive lateral⁽¹⁾ interaction between the inhibitor molecules containing long hydrocarbon chains due to Vander Waals forces give rise to stronger adsorption and higher inhibition efficiency as in CA plant extract.

Therefore, it could be concluded that CA plant extract acts as excellent corrosion inhibitor for Al-Cu alloy in 2M HCl solution.

Conclusion:

1) Corrosion rate of Al-Cu alloy in acidic media decreases in the order :



2) CA displayed higher inhibitive properties towards the corrosion of Al-Cu alloy in 2M HCl solution in temperature range 25 – 65°C

3) The physical adsorption behaviour of CA in acidic media is in agreement with the Flory – Huggins and thermodynamic/kinetic model, one molecule of inhibitor occupying more than one active site.

4) Polarization studies show that CA extract acts as cathodic – type inhibitor.

5) The results of EIS indicate that values of R_{ct} and IE% increase with increasing the inhibitor concentration.

6) There is a great agreement between the results obtained by different techniques of measurements.

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