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Inhibition of Aluminum Corrosion in Acid Medium by Cassia Acutifolia Extract.

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Abstract

The inhibitive effect of aqueous extract of Cassia acutifolia leaves toward the corrosion of aluminum in 1 MHCl solution has been investigated by weight loss measurements, galvanostatic, potentiodynamic anodic polarization techniques and electrochemical impedance spectroscopy technique. It was found that Cassia acutifolia extract act as a good inhibitor for aluminum corrosion in the acid solution. The inhibition action of the extract it was discussed in view of the adsorption of its components on aluminum surface. It was found also that the adsorption is a spontaneous process and follows Langmuir adsorption isotherm. The inhibition efficiency (%IE) increase as the extract concentration increased. Moreover, the effect of temperature on the (%IE) was studied. The (%IE) decrease with increased the temperature. It was found that the presence of extract increases the activation energy of the corrosion reaction. Moreover, the thermodynamic parameters of adsorption process were calculated. It was found also that the extract provides a good protection to aluminum against pitting corrosion in chloride ion containing solutions.

1- Introduction

Corrosion is the destructive attack on a metal or metal alloy by chemical or electrochemical reaction with its environment [1]. Aluminum has an economic and industrial importance due to lightweight, high thermal and electrical conductivity. The resistance of aluminum against corrosion in aqueous media can be attributed to a rapidly formed compact, strongly adherent and continuous oxide film [2, 3].Therefore, aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries. In some cases, aluminum may be exposed to high concentrations of acids or bases. The solutions dissolved the passive film. In addition, aluminum may be used in neutral solutions containing pitting agents such as chloride ions. These solutions cause pitting corrosion. Under these circumstances, corrosion inhibitors should be used [4, 12]. Most of corrosion inhibitors are synthetic chemicals which are toxic, expensive and non-biodegradable. Green corrosion inhibitors have become important because they are ecofriendly and cheap .Plant extracts are viewed as an incredibly rich source for naturally synthesized chemical compounds that can be extracted by simple procedure with low cost [13, 21].

On this note, ethanol or aqueous extracts of some plants have been found to be good corrosion inhibitors for some metals (notably Aluminum, Mild steel and Zinc). Therefore, the present study is aimed to investigating the corrosion inhibit properties of Cassia acutifolia extract for aluminum in 1M HCl by using weight loss measurements, potentiodynamic anodic polarization, galvanostatic techniques and electrochemical impedance spectroscopy technique.

2- Experimental

2.1. Materials and medium

Aluminum metal with purity 99.95% provided by the (Aluminum Company of Egypt, Nagh Ammady) was studied in the present work. For weight loss measurements, corrosion inhibition tests were performed using coupons with surface area 3 cm^2.the aluminum coupons were polished with emery papers, then degreased with acetone and washed with distilled water. For electrochemical measurements, a cylindrical rod embedded in araldite .The electrodes used were polished with different grades of emery papers, then rinsed with acetone, distilled water, and finally dipped in the electrolytic cell. All solutions were prepared from analytical grade chemical reagents using doubly distilled water.

2.1.1 Extract preparation

Fresh leave of Cassia acutifolia were extensively washed to remove dust particles, then washing by distilled water .they were further air dried on filter paper at room temperature and then powdered with the help of sterilized pestle and mortar. Dry powder was further extracted by using aqueous solvent.

Air dried powder of respective plant part was mixed well in 100ml distilled water and kept at room temperature for 24 h on an orbital shaker with150ppm. The supernatant thus obtained was filtrated through Whitman's filter no.1, and then the filtrate was evaporated until decreases. The solid residue was collected and used in preparation of stock solution from which the desired concentration were prepared by dilution. The extract main component has the formulas shown in Fig.1.

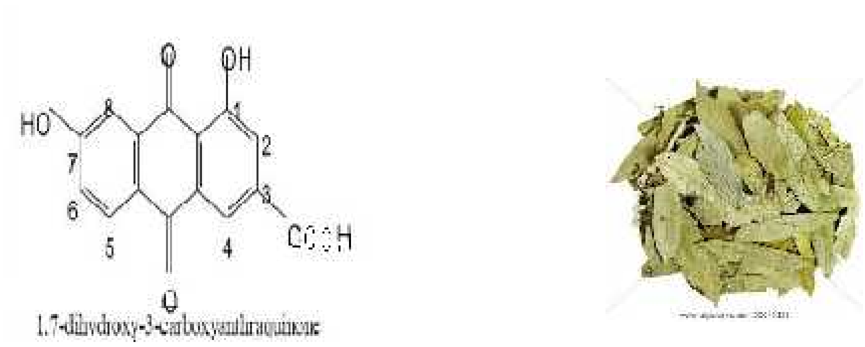

Fig (1): The major component of cassia acutifolia [22]

RESULTS AND DISCUSSION

3.1. Weight loss measurements.

In weight loss experiment, clean (Al) coupons were weight and immersed completely in the corrodent in the presence and absence of inhibitors .the weight loss (g/cm^2) was determined at different immersion times at 30^0c by weighting the cleaned samples before and after immersion into 100 ml of solutions. The weight loss and percentage inhibition efficiency were calculated according to the following equations:-

$$\Delta W=W_1-W_2 \qquad (1)$$

Where W_1 and W_2 are the weights of specimen before and after reaction respectively.

$$\%I.E= (\Delta W-\Delta W_i/\Delta W) \times 100 \qquad (2)$$

Where ΔW and ΔW_i are the weight losses per unit area in absence and presence of the additive, respectively.

Fig (2) show the weight loss – time curves for aluminum coupons in 1M HCl solution in absence and presence of different concentrations of extract at 30^0c. The values of weight loss and inhibition efficiency at different times are listed in table (1).It has been found that the inhibition efficiency increased with increase inhibitors concentrations, indicating that extraction acted as good inhibitor.

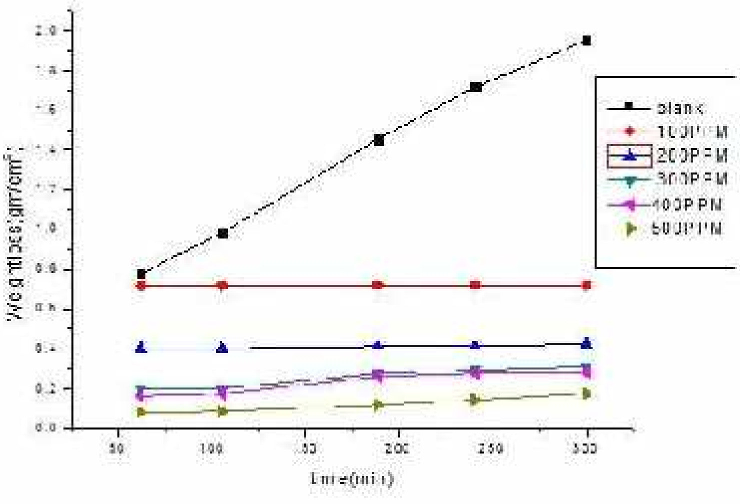

Fig (2): Weight loss-time curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of Cassia acutifolia.

3.2. The effect of temperature and activation parameters

The effect of temperature on the corrosion rate of Al in 1MHCl solution containing 500ppm of extract was studied using weight loss measurements over temperature rang 30-60^{0}C.

The effect of temperature rising on the values of inhibition efficiency are listed in table (2) and Fig (3) contains weight loss-time curves for the corrosion of aluminum in 1 M HCl in the presence 500PPM of Cassia acutifolia at different temperatures. It has been found that the temperature increases the weight loss increase and hence the inhibition efficiency decrease. This result suggests a physical adsorption of the extract compounds on the aluminum surface.

Table (1) : Wt. loss (mg.cm $^{-2}$) of aluminum corrosion in 1M HCl solution devoid of and containing different concentration of Cassia acutifolia at different exposure times.

T, h	Free	100	%I.E	200	%I.E	300	%I.E	400	%I.E	500	%I.E
1	0.7371	0.7188	2.49	0.4213	42.85	0.3101	57.93	0.2813	61.84	0.1735	76.47
2	0.9956	0.7186	27.83	0.4117	58.56	0.2934	70.54	0.2757	72.31	0.1421	85.73
3	1.7652	0.7182	59.32	0.4101	76.77	0.2748	84.44	0.2597	85.29	0.1152	93.50
4	1.8891	0.7175	62.02	0.3998	78.84	0.1998	89.43	0.1731	90.84	0.0832	95.60
5	1.9575	0.7169	63.38	0.3987	79.64	0.1987	89.85	0.1599	91.84	0.0798	95.93

Table 2: Percentage of inhibition efficiency of aluminum dissolution in 1 MHCl in the presence of 500ppm of inhibitor concentrations at different temperatures and at 300 min immersion.

Temperature, K	Cassia acutifolia
303	95.93
313	84.39
323	81.40
333	79.25

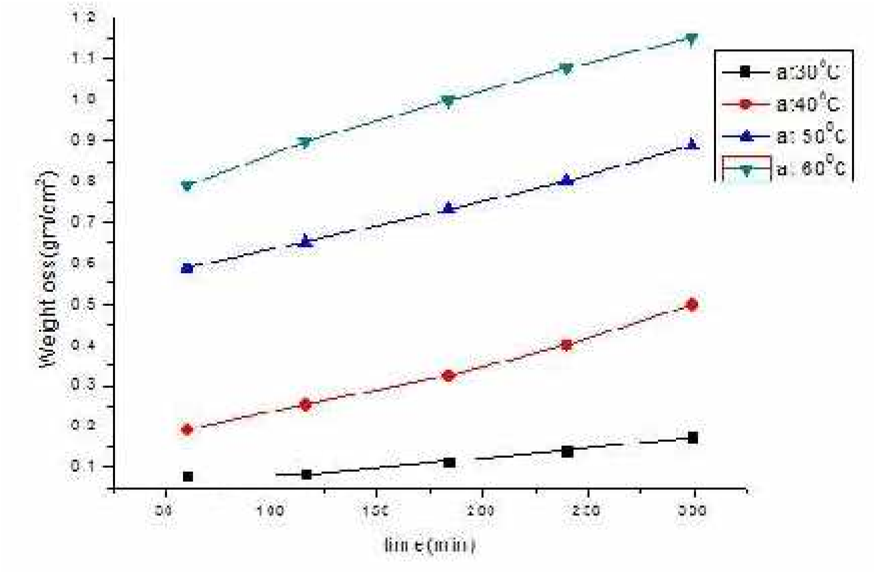

Fig (3): Weight loss-time curves for the corrosion of aluminum in 1 M HCl in the presence 500PPM of Cassia acutifolia at different temperatures.

The apparent activation energy Ea* , the enthalpy of activation ΔH* and the entropy of activation ΔS* for the corrosion of aluminum samples in 1MHCl solution in absence and presence 500 ppm of inhibitors were calculated from Arrhenius –type equation[23]:

$$K=A\exp(-Ea^*/RT) \qquad (3)$$

and transition- state equation:

$$K=RT/Nh \exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (4)$$

Where K is corrosion rate, A is frequency factor, h is plank's constant, N is Avogadro's number and R is the universal gas constant. A plot of log rate vs. 1/T (Fig4) give straight lines with slope of –Ea*/2.303R.

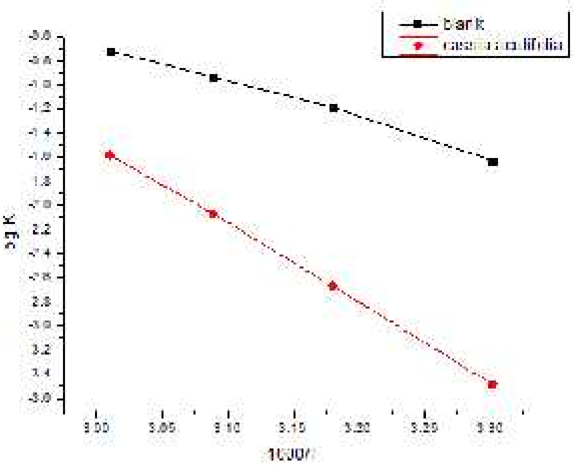

Fig (4): log corrosion rate -1/T –curves for aluminum dissolution in 1MHCl in absence and presence of 500ppm of additive.

Fig (5): represent plots of the log rate log rat/ T vs. 1/T are obtained straight lines with slop of (-ΔH*/2.303R) and intercept of log (RT/Nh)-(ΔS*/2.303R).

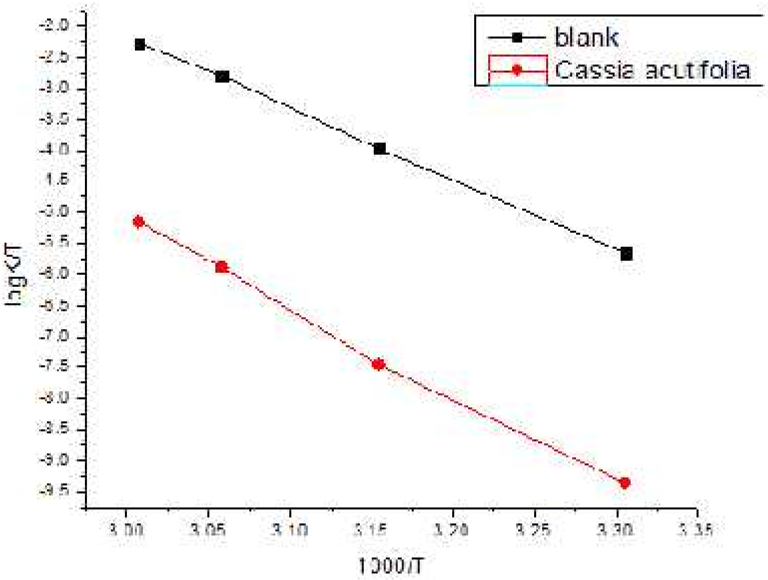

Fig (5): log (corrosion rate/T) – (1/T)–curves for aluminum dissolution in 1MHCl in absence and presence of 500ppm of additive.

The calculated values of the apparent activation energy, Ea*, activation entropies, ΔS* and activation enthalpies, ΔH* are given in table (3).

Table 3: Activation parameters of aluminum dissolution in1M HCL solution in the absence and presence of 500 ppm additive.

Inhibitors	Activation parameters		
	Ea * , k J mol^{-1}	Δ H * , KJ mol^{-1}	-Δ S*, J mol^{-1} k^{-1}
Free acid	27.94	144.24	1029.14
Cassia acutifolia	353.71	302.06	799.84

From the results of Table (3), it is clear that the presence of the tested compounds increases the activation energy values and consequently decreased the corrosion rate of the aluminum. These results indicate that these tested compounds act as inhibitors through increasing activation energy of aluminum dissolution by making a barrier to mass and charge transfer by their adsorption on aluminum surface. The positive signs of ΔH* reflect the endothermic nature of the aluminum dissolution process.

The negative values of ΔS* in the absence and presence of the inhibitors implies that, the activated complex is the rate determining step and represents association rather than dissociation.

3.3. Galvanostatic Polarization Technique.

Fig (6) represents the anodic and catholic polarization curves of aluminum electrode in 1MHCl solutions containing different concentrations of additives. Inspection of Fig.6 reveals that, both anodic and catholic polarization curves are shifted to less current density values in presence extract.

The values of corrosion current density (I_{corr}) were determined by the intersection of the extrapolated catholic and anodic Tafel lines (linear part) with the stationary corrosion potential (E_{corr}).

The percentage inhibition efficiency (% I.E) imparted by the added inhibitor, which is defined as the percentage of the relative decrease in corrosion rate brought about by the presence of a certain concentration of the inhibitor is given by:-

$$\% \text{ I.E} = (1 - I_{add} / I\ f_{ree})\ x100 \qquad (5)$$

Where, Ifree and Iadd are the corrosion current densities in the absence and presence of the inhibitors, respectively.

Tables (4) show the effect of different concentrations of extract on the corrosion parameters such as: cathodic Tafel slop (bc), anodic Tafel slop (ba), corrosion potential (Ecorr), corrosion current density (Icorr), percentage inhibition efficiency (%I.E) and surface coverage (θ). From table (4) , it can be observed that (Icorr) decreased significantly after the addition of Cassia acutifolia .The (%I.E) increased with the increase in the Cassia acutifolia concentrations .The values of cathodic Tafel slope (bc) and anodic Tafel slop (ba) does not change significantly with the increase in the Cassia acutifolia concentrations .This indicates that the addition of Cassia acutifolia does not change the hydrogen evolution reaction mechanism and its non-interference of inhibitor in the mechanism of anodic reaction [24]. From table (4) it is obvious that there is no appreciable shift in the corrosion potential values (Ecorr) after the addition of inhibitors ,which indicates that inhibitor is mixed type inhibitor [25].

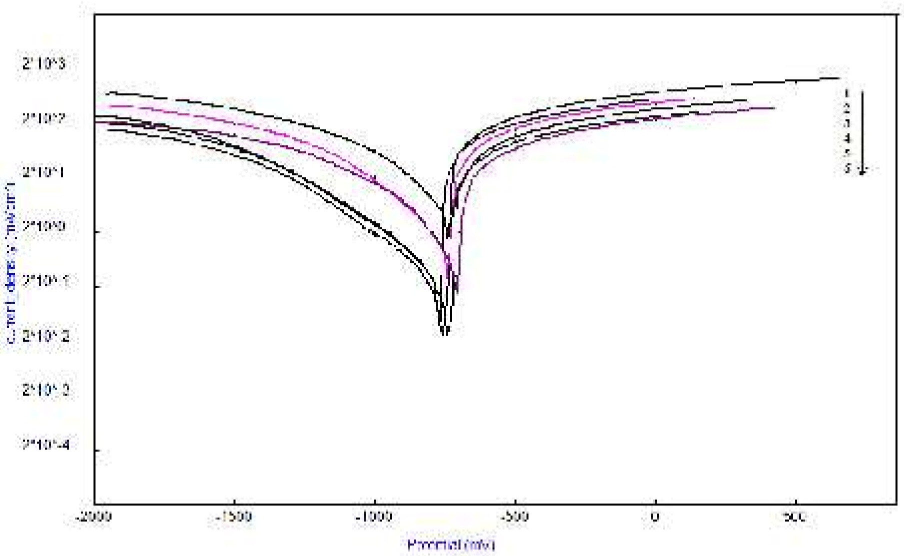

Fig (6): Galvanostatic polarization curves of aluminum in 1MHCl containing different concentrations of Cassia acutifolia. (1) 0.00 (2)100 (3) 200 (4) 300 (5) 400 (6) 500 ppm.

Table (4): Corrosion parameter obtained from galvanostatic polarization measurements of aluminum in 1M HCl solution containing different concentrations of Cassia acutifolia.

Conc. (ppm)	b_a mV dec^{-1}	$-b_c$ mV dec^{-1}	$-E_{corr}$ mV (SCE)	I_{corr} (mA cm^{-2})	θ	%I.E
0	172.06	193.112	746.8	5.393	---------	---------
100	90.01	189.53	756.3	1.6557	0.6930	69.30
200	47.54	160.62	753.1	1.2193	0.7740	77.40
300	43.49	192.72	790.1	0.6756	0.8748	87.48
400	70.07	175.39	721.5	0.2491	0.9538	95.38
500	57.80	177.06	765.8	0.1840	0.9660	96.60

3.4. Adsorption isotherm

The inhibiting effect of inhibiting compound is manifested as result of their adsorption on the surface of aluminum. The chemical structure of compound ,nature and charge of the metal surface ,nature of corrosion medium and it's PH value , the temperature, and the electrochemical potential of the metal- solution interface.

The surface coverage (θ) which represents the represents the part of the metal surface covered by the inhibitor molecules was calculated using the following equation:

$$\theta = 1- I_{add} / I_{free} \quad (6)$$

Where, I_{free} and I_{add} are the corrosion current densities in absence and presence of the additive compounds, respectively

The results are best fitted by Langmuir adsorption isotherm according to the following equation:-

$$C/\theta = 1/k + C \qquad (7)$$

Where K and C are the equilibrium constant of adsorption process and additive concentration, respectively.

The equilibrium constant of adsorption K is related to the standard free energy of adsorption by the relation(8):

$$K = 1/55.5\exp(-\Delta G^{o}_{ads}/RT) \qquad (8)$$

Where R is universal gas constant, the value 55.5 is the concentration of water in the solution in mole / liter and T is the absolute temperature. The values of K and ΔG^{o}_{ads} of the inhibitors adsorbed on the surface of aluminum were calculated and listed in Table (5).

The standard free energy of adsorption is associated with water adsorption / desorption equilibrium which forms an important part in the overall free energy change of adsorption. The negative values of ΔG^{o}_{ads} obtained indicate that the adsorption process of these compounds on the metal surface is spontaneous.

Fig (7) shows the Langmuir adsorption plots for adsorption of inhibitor on the surface of aluminum in 1MHCl acid at 30°C. The data gave straight lines indicating that Langmuir isotherm is valid for this system.

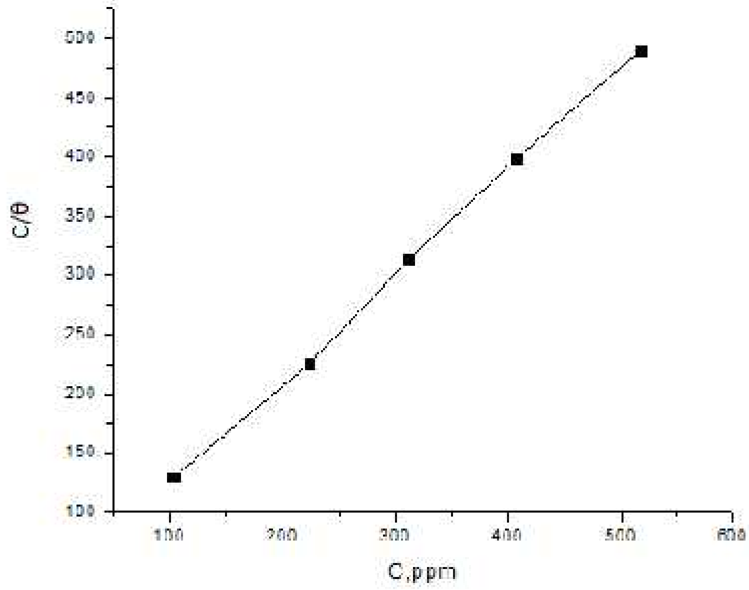

Fig (7): Curve fitting of corrosion data for aluminum in 1MHCl in presence of different concentrations of inhibitor to Langmuir isotherm at 30 °C.

Table (5): Equilibrium constant and the adsorption free energy of natural compounds adsorbed on the surface of aluminum electrode in 1 M HCl.

Inhibitor type	K	$-\Delta G^{o}_{ads}$
Cassia acutifolia.	0.024	192.26

3.5. Inhibition of Pitting Corrosion of aluminum

Fig.8 represents the of potentiodynamic anodic polarizations curves of aluminum electrode in 1M HCl+ 0.5M NaCl (as a pitting corrosion agent) in absence and present of different concentrations of inhibitor at a scanning rate of $1mVsec^{-1}$.The potential was swept from negative potential toward anodic direction up to the pitting potential (E_{pitt}.).The pitting potential was taken as the potential at which the current flowing, along the passive film increases suddenly to higher values, denoting the destruction of passive film and initiation of visible pits. It was found that the pitting potential of the aluminum electrode is shifted to more positive (noble) values with increasing the concentration of these additives. This indicates that increased resistance to pitting attack [26].

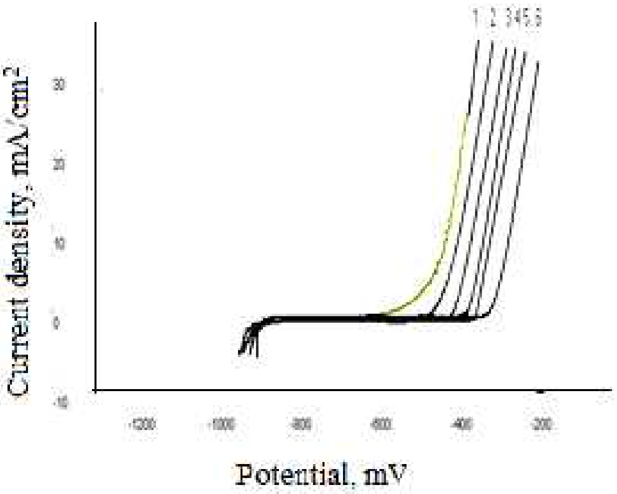

Fig (8): Potentiodynamic anodic polarization curves of aluminum in1M HCl solution +0.5M of NaCl containing different concentrations of Cassia acutifolia.

Fig (9) represents the relationship between pitting potential and the logarithmic of the molar concentration of the added Compound. Straight lines were obtained and the following conclusion can be drawn:-

The increase of inhibitor concentration causes the shift of the pitting potential into more positive values in accordance with the following equation:

$$E_{pitt.} = a_1 + b_1 \log Cinh. \qquad (9)$$

Where, a_1 and b_1 are constants which depend on both the composition of additives and the nature of the electrode.

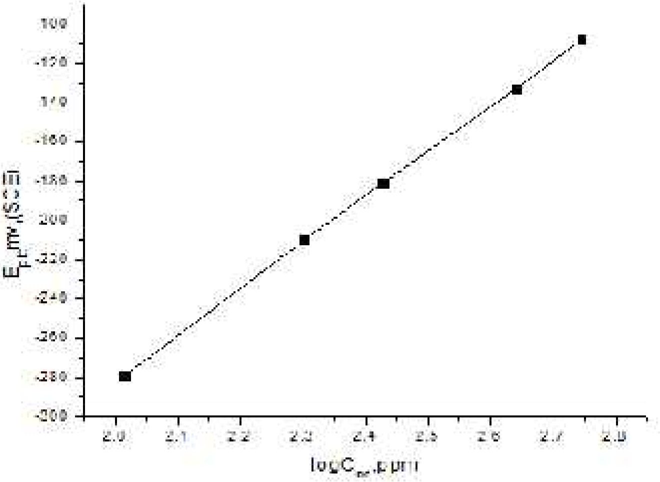

Fig (9): The relationship between the pitting potential of aluminum and logarithm the concentration compound in presence 0.5 M NaCl solution.

3.6. Electrochemical impedance measurements.

The results of impedance parameters (R_{ct} and C_{dl}) for inhibitor are given in fig (10). It can be seam from the fig (10) that the charge transfer resistance (R_{ct})value increase with increase in inhibitor concentrations but the value of double layer capacitance (C_{dl}) decrease due to decrease in local dielectric constant and increase in thickness of the electrical double layer, suggesting that the inhibitor molecules function by adsorption at the metal solution interface. Hence the inhibition efficiency increases with increase inhibitor concentrations, these results are recorded in table (6), which show the effect of different concentrations of extract on the corrosion parameters such as Rct charge transfer resistance, Cdl double layer capacity, φ surface coverage, and %I.E inhibition efficiency .

The impedance plots recorded for the corrosion of the Al in the presence of Cassia acutifolia were modeled by using the equivalent circuit depicted in Fig (11). EC-lab version 10.30, model : sp 150,Which the inhibition efficiency were calculated from equation (10),where R_{ct}^0 and R_{ct} arecharge transfer resistance in absence and presence inhibitor respectively.

$$\%I.E = (1- R_{ct}^0/ R_{ct})\times 100. \qquad (10)$$

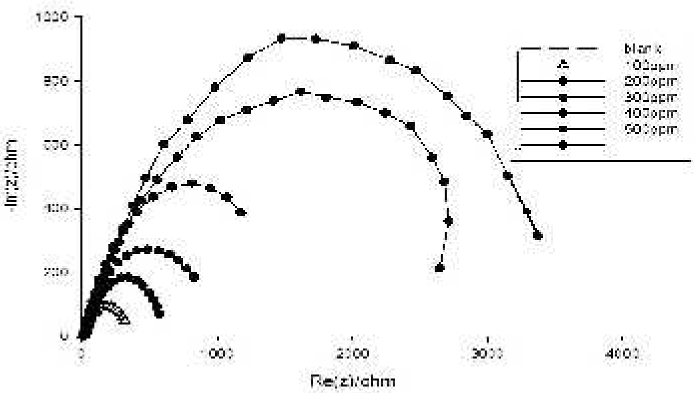

Fig (10): Nyqist plots of Al in 1M HCl in absence and presence of different concentrations of Cassia acutifolia.

Table (6): Electrochemical parameters obtained from EIS measurements of Al in 1M HCl at various concentrations of Cassia actufolia.

Conc. (ppm).	Rct (Ω cm^2)	Cdl (F.Cm^{-2})	ɷ	I.E%
Blank	353	4.261*10-3	-	-
100	6045	2.488*10-3	0.4171	41.71
200	990	2.252*10-3	0.6452	64.52
300	1541	0.3172*10-3	0.7711	77.11
400	2832	0.1631*10-3	0.8854	88.54
500	3331	4.036*10-6	0.9841	89.41

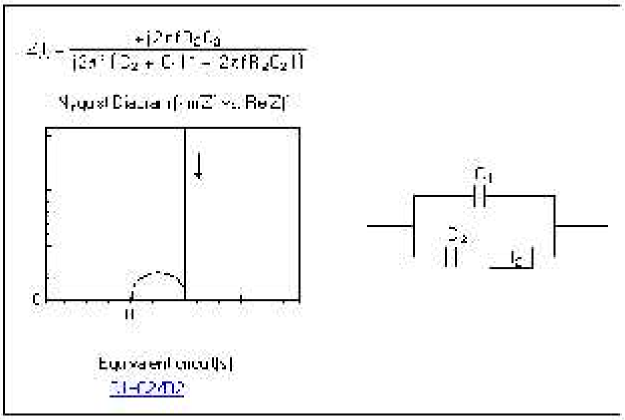

Fig (11): Equivalent circuit used to fit the experimental EIS data for the corrosion 0f Al in the presence of different concentrations of Cassia actufolia.

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