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Inhibition of Acid Aluminum Corrosion in Presence of Aqueous Extract of Domiana

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Abstract

The inhibitive effects of the aqueous extract of Domiana (turnera Aphrodisiacal) for The Corrosion of aluminum in 1 M HCL Solution was investigated using weight loss measurements, galvanostatic, potentiodynamic anodic polarization techniques and elecrochemical impedance spectroscopy technique. The results drawn from these techniques indicate that the inhibition efficiency increase with the concentration of inhibitors increase but decrease with temperature. Inhibition was explained in term of the adsorption of the extract on the aluminum surface. The adsorption process is fitting Langmuir adsorption isotherm. It was found that extract protect aluminum surface from pitting attack in chloride containing solution by shifting the pitting corrosion potential to more noble direction .

1. Introduction

Aluminum (Al) and it's alloys are widely used in many industries such as house hold applications due to their corrosion passivity in neutral media and atmospheric conditions due to formation of passive oxide layer on them Hydrochloric acid solutions are used for pickling, chemical and electro chemical etching of aluminum [1].

Moreover, the presence of aggressive ions like chloride creates extensive localized attack [2].

One of the most practical Methods for protection of metal against corrosion in acidic solution is use of organic compounds [3-11]. The inhibition action of these compounds is due to the adsorption on the metal surface.

The adsorption process depend on mainly on certain phyisco-chemical properties of the molecules such as functional groups, steric factors, aromaticity, electron- density at the donor atoms, TT-orbital's character of donating electrons [12-13] and also on the electronic structure of the molecules.

The major problem is that The Most of corrosion inhibitors are not ecofriendly, Toxic, and expensive. Plant extracts have become important because they are ecofriendly and cheap. Natural products were previously used as corrosion inhibitors for different metals in various environments [14-24] and their optimum concentrations were reported.

The present work devotes to investigate the effect of Domianaa (Turnera Aphrodisiacal) extract as corrosion inhibitors for aluminum in 1 M HCL 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 3cm^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 Domianaa (turnera aphrodisiacal) 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.

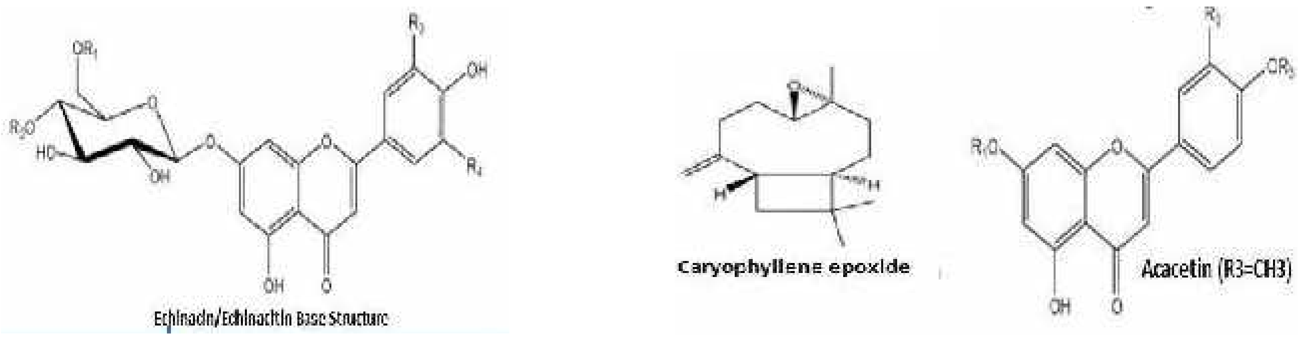

Fig.1. Major Components of domianaa

3. 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^{0}c 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^{0}c. 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.

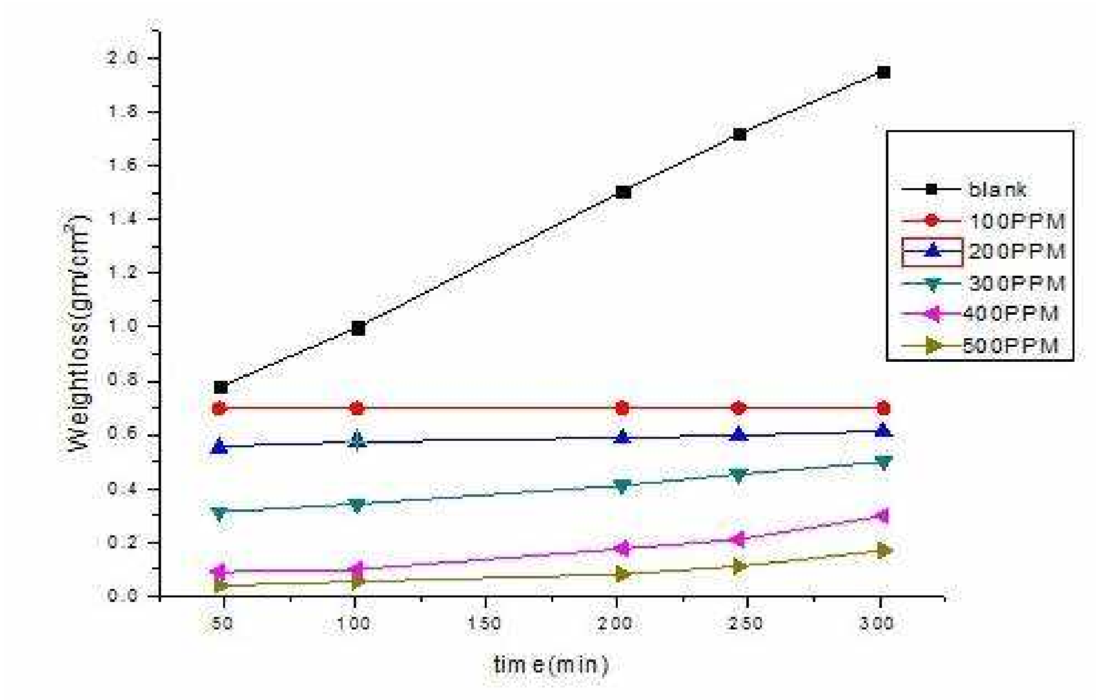

Fig (2): Weight loss-time curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of Domiana (Turner Aphrodisiacal).

Table (1) Data of aluminum corrosion in 1M HCl solution devoid of and containing different concentration of Domiana (Turnera Aphrodisiacal) at different exposure times.

t,h	Free	100ppm	%I.E	200ppm	%I.E	300ppm	%I.E	400ppm	%I.E	500ppm	%I.E
1	0.7371	0.6985	5.24	0.6152	16.54	0.4992	32.28	0.2983	59.54	0.1699	76.95
2	0.9956	0.6983	29.86	0.5997	39.76	0.4531	54.49	0.2112	78.79	0.1431	85.63
3	1.7652	0.6981	60.45	0.5871	66.75	0.4117	76.68	0.1761	90.03	0.0812	95.40
4	1.8891	0.6978	63.06	0.5772	69.45	0.3769	80.05	0.0967	94.88	0.0538	97.15
5	1.9575	0.6973	64.38	0.5532	71.74	0.3132	84.00	0.0898	95.42	0.0389	98.02

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) Weight loss-time curves for the corrosion of aluminum in 1 M HCl in the presence 500PPM of Domiana (Turner Aphrodisiacal)at different temperatures. It has been found that the temperature increases the weight loss increase and hence the inhibition efficiency decrease. Thisresult suggests aphysical adsorption of the extract compounds on the aluminium surface.

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	IE%
303	98.02
313	92.55
323	91.26
333	90.40

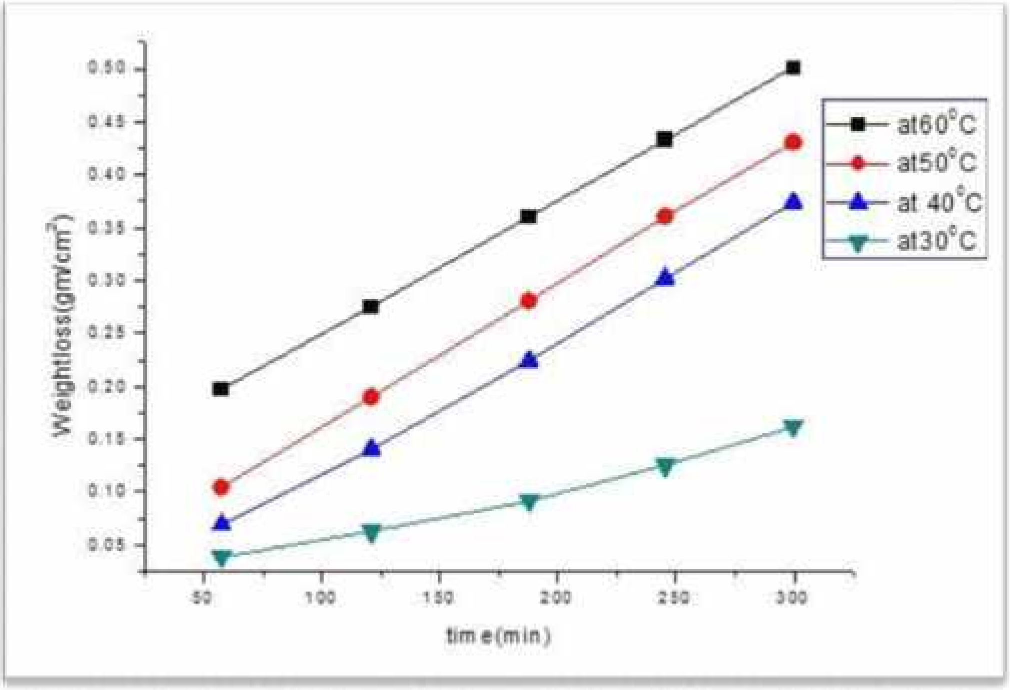

Fig (3): Weight loss-time curves for the corrosion of aluminum in 1 M HCl in the presence 500PPM of Domiana (Turnera Aphrodisiacal) at different temperatures.

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[25].

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

And transition- state equation:

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

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.

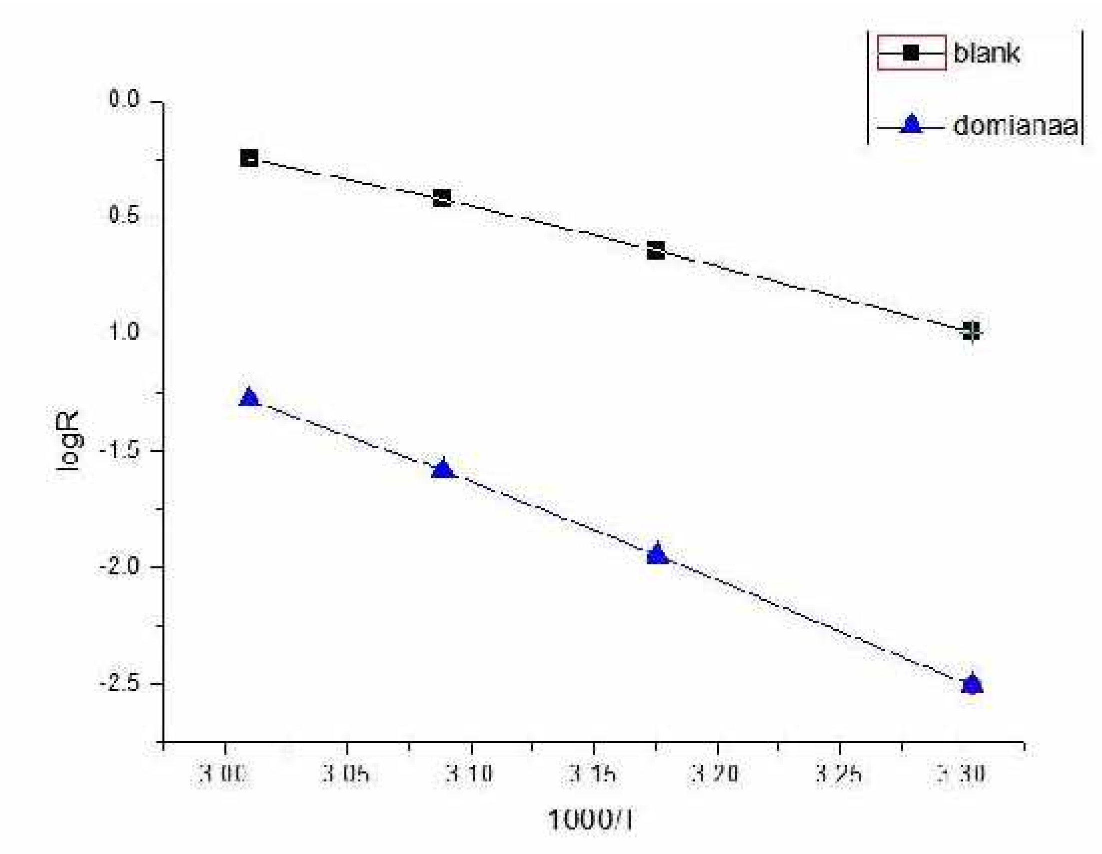

Fig (4): log corrosion rate -1/T –curves for aluminum dissolution in 1MHCl in absence and presence of 500ppm of additive.

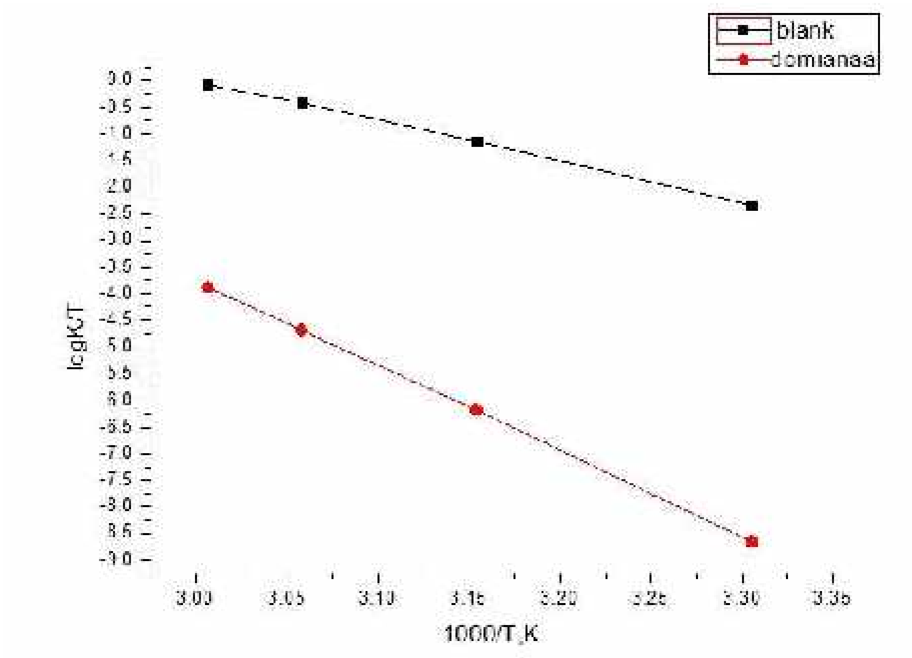

Fig (5): log (corrosion rate/T) – (1/T)–curves for aluminum dissolution in 1MHCl in absence and presence of 500ppm of additive.

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).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 of500 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
Domianaa	278.10	275.55	856.68

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**.**

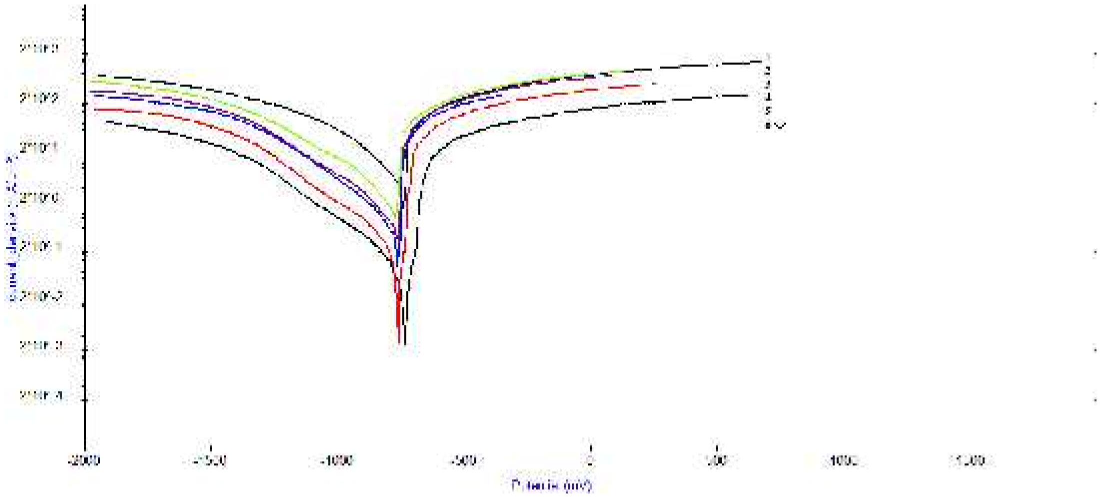

Fig (6) Galvanostatic polarization curves of aluminum in 1MHCl containing different concentrations of Domiana (Turnera aphrodisiaca). (1)0.00ppm (2)100PPM (3)200PPM (4)300PPM (5)400PPM (6)500PPM.

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:-

$$\% \text{ I.E} = (1 - I_{add} / I_{free}) \times 100 \qquad (5)$$

Where, I_{free} and I_{add} 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: catholic Tafel slop (bc), anodic Tafel slop (ba), corrosion potential (E_{corr}), corrosion current density (I_{corr}), percentage inhibition efficiency (%I.E) and surface coverage (θ).An inspection of this table, it is clear that the corrosion potentials (E_{corr}) is shifted to more negative values and Tafel lines are shifted to more positive and negative potential for anodic and catholic process, respectively, relative to the blank curve. This means that this extract influence both anodic and cathodic process. However, the data suggested that these compounds act mainly as mixed type inhibitors. The values of anodic and catholic Tafel slopes (ba & bc) are approximately constant which suggest the simple blocking of the available surface area of the metal by the inhibitor molecules.

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

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	117.541	5.393	----------	---------
100	100.7353	174.049	47.505	2.179	0.5960	59.60
200	91.266	170.194	39.871	1.829	0.6611	66.11
300	87.351	168.145	29.941	1.013	0.8490	84.90
400	67.421	160.153	20.831	0.811	0.8496	84.96
500	53.012	147.386	12.871	0.0773	0.9856	98.56

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 P^H 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:

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

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) plot of (C /φ) vs. C (Langmuir adsorption plots) for adsorption of inhibitor on the surface of aluminum in 1MHCl acid at 30^0c.

The data gave straight lines indicating that Langmuir isotherm is valid for this system.

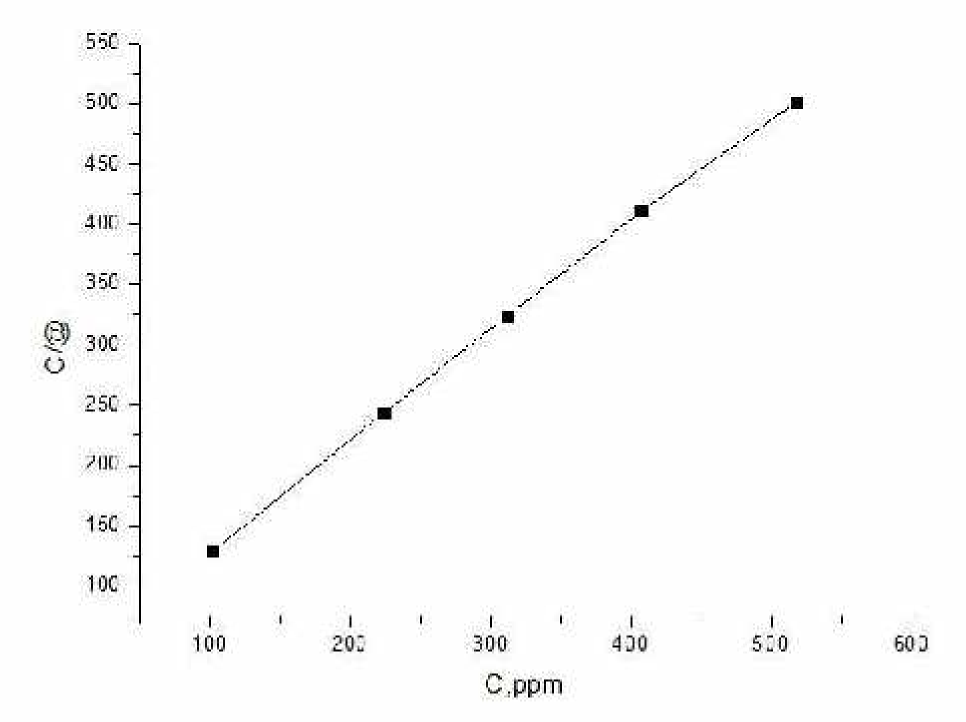

Fig (7) Curve fitting of corrosion data for aluminum in 1MHCl in presence of different concentrations of inhibitor to Langmuir isotherm at 30^0c.

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	$-\Delta G^O_{ads}$
Domiana(Turnera aphrodisiacal)	0.023	193.40

3.5. Inhibition of Pitting Corrosion of aluminum

Fig.8 re presents 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].

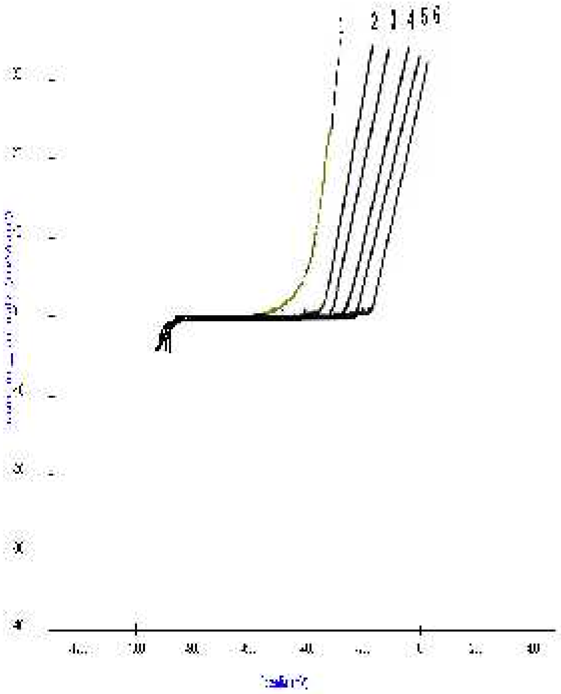

Fig. (8)Potentiodynamic anodic polarization curves of aluminum in1M HCl solution +0.5M of NaCl containing different concentration of Domiana (Turnera aphrodisiacal).

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:

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

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

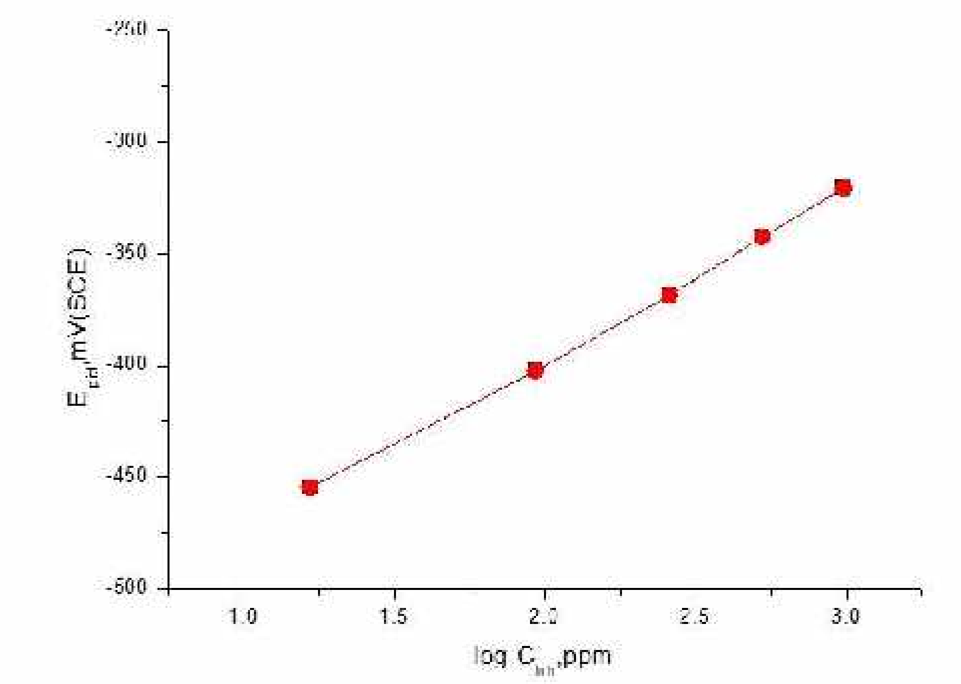

Fig. 9: The relationship between the pitting potential of aluminum and logarithm the concentration compound in presence 0.5 M NaCl solution**.**

3.6. Electrochemical impedance measurements.

The inhibition efficiencies of Domiana (Turnera aphrodisiacal) on aluminium were examined by electrochemical impedance spectroscopy . The impedance spectra of aluminium in 1 MHCl solution in the absence and presence of different concentrations of Domiana (Turnera aphrodisiacal) were recorded Fig(10). shows the impedance spectra in Nyquist format.The impedance diagrams display one single capacitive loop represented by slightly depressed semi-circle for all studied compounds . This capacitive loop indicates that the corrosion of aluminium in1 M HCl solution is mianly controlled by charge transfer process and formation of aprotective layer on the metal surface. Deviations from the ideal semi-circle are generally attributed to the frequency dispersion as well as in homogeneities, roughness of metal surface and mass transport process[27-29] .The impedance response of aluminum in HCl changes with the addition of Domiana (Turnera aphrodisiacal) into the test solutions and this changes more pronounced with increasing inhibitor concentration . The diameter of the capacitive loop increases as the concentration of inhibitor rises, this increase indicates adsorption of inhibitor molecules on the metal surface [30].On the other hand, the similar nature of the impedance diagrams obtained in the absence and presence of Domiana (Turnera aphrodisiacal) reveal that the addition of inhibitors does not change the mechanism for the dissolution of aluminum in HCl[31-33].

The impedance plots recorded for the corrosion of the Al in the presence of Domiana (Turnera aphrodisiacal) were modeled by using the equivalent circuit depicted in Fig(11). EC-lab version 10.30, model : sp 150 The results recorded from Table(6) indicated the increase of R_{ct} value and inhibtion efficiencies with the increase in the concentrations of the inhibitor. This suggests that the amount of the inhibitors molecules adsorbed on the electrode surface increases as the concentration of Domiana (Turnera aphrodisiacal) increases,Where The inhibtion efficiencies were calculated from equation (10),Where R_{ct} and R_{ct}^0 are the charge transfere resistance of Al with and without inhibtors, respectively . The decrease in C_{dl} could be attributed to the decrease in local dielectric constant and /or an increase in the thickness of the electrical double layer, signifying that the Domiana (Turnera aphrodisiacal)molecules act by adsorption at the interface of metal / solution.

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

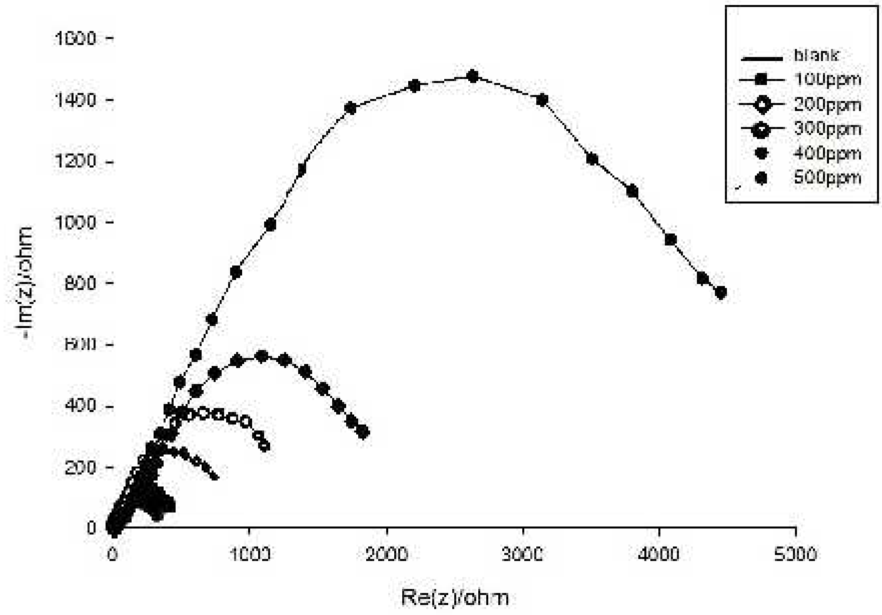

Fig.10: Nyqist plots of Al in 1M HCl in absence and presence of different concentrations of the Domiana (Turnera aphrodisiacal).

Table(6):- Electrochemical parameters obtained from EIS measurements of Al in 1M HCl at various concentrations of Domiana (Turnera Aphrodisiaca).

Conc (ppm).	R_{ct} (Ω cm^2)	C_{dl} ($F.Cm^{-2}$)	ɷ	I.E%
Blank	353	$4.261*10^{-3}$	-	-
100	447	$3.522*10^{-3}$	0.2110	21.10
200	851	$3.121*10^{-3}$	0.5851	58.51
300	1387	$0.3992*10^{-3}$	0.7455	74.55
400	2028	$0.2652*10^{-3}$	0.8262	82.62
500	5002	$2.066*10^{-6}$	0.9295	92.95

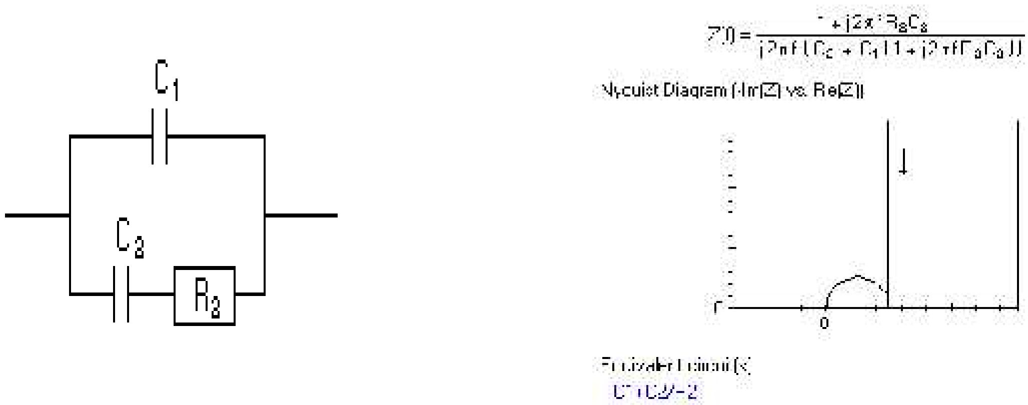

Fig.11:Equivalent circuit used to fit the experimental EIS data for the corrosion 0f Al in the presence of different concentrations of Domiana (Turnera aphrodisiacal).

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