ZIZIPHUS SPINA – CHRISTI AS GREEN CORROSION INHIBITOR FOR AL-CU ALLOY IN ACIDIC AND ALKALINE MEDIA.

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Abstract

Ziziphus Spina – Christi extract (ZSC) was investigated as green corrosion inhibitor for Al-Cu alloy in acidic and alkaline media using chemical and electrochemical techniques. The weight loss results were interpreted by means of the kinetic –thermodynamic isotherm of extract adsorption on the alloy surface. The values of ΔG°_{ads} ranged from -5.08 to -23.43 kJ/mol revealed a strong physical and spontaneous adsorption of the ZSC on the alloy surface. The higher inhibition efficiency about 91.08% and 85.60% was observed at 8.0 g/L in 2.0M HCl and 1.5M NaOH. Activation parameters, E_a^{*} , ΔH^{*} and ΔS^{*} supporting the proposed physisorption mechanism. Potentiodynamic polarization measurements showed that the presence of ZSC extract in both media affects mainly the cathodic process, and decreases the corrosion rate to a great extent. The results obtained from weight loss and thermometric measurements are in a good agreement with potentiodynamic polarization measurements.

Keywords: Al alloy corrosion, Ziziphus Spina-Christi extract, inhibitor, and adsorption.

Introduction :

The protection of the metal or alloys against corrosion can be achieved either by special treatment of the medium to depress its aggressiveness or by introducing into small amounts of special substances called corrosion inhibitors. Most of researches were devoted to study the corrosion inhibition of metal and its alloys in aqueous media using large number of organic compounds [1-10]. Recently started to study the natural compounds of some plant extracts as green corrosion inhibitors [11-15] with low risk of environmental pollution. This extract contains different hydroxy organic compounds, e.g. tannins, flavoniods, anthraquinones, steroids, saponins and other nitrogen containing compounds.

There are no reports in the literature on the use of the plant extract of Ziziphus Spina-Christi (ZSC) therefore; the aim of the present work is to examine the effect of (ZSC) as green corrosion inhibitor for Al-Cu alloy in acidic and alkaline media, using chemical and electrochemical measurements.

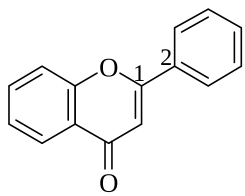
Experimental

The surface analysis for aluminum – copper alloy was presented in Table (1). Al alloy sheets with dimension of 3.0x1.0x0.2 cm were used for weight loss and thermometric measurements. For polarization a cylindrical rod was mounted into glass tube by epoxy resin, with exposed surface area of 1.68 cm^2 to contact the solution. 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.

Table (1): Elemental analysis for Al-Cu alloy (w%).

Al	Cu	Fe	Mn
94.750	3.980	0.725	0.550

The electrolytic solutions HCl, H_3PO_4 ,H_2SO_4 and NaOH were prepared using Analar grade reagents. Preparation of the plant extract [16], ZSC Fig (1) is carried out by boiling weighed amounts of the crused seeds of the plant. After filtration, the liquid was evaporated in an oven at 50ºC for 48 hours. Crystalline precipitate is formed and the concentrations are expressed as w/v.



(Flavonoide)

Fig (1): The main chemical structure of Ziziphus spina-christi.

Weight loss measurements were recorded by the usual procedure [17] at temperature range (25-65ºC) with and without different concentrations of the plant extract. Triplicated samples were used to check reproducibility of results. Corrosion rates (C.R.) were expressed in g/cm^2 min, and the inhibition efficiency percentage (*IE%*) was calculated from the relationship[18]:

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

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

Thermometric measurements were described by Mylius [19]. Each experiment was carried out with 15ml of test solution. The initial temperature in all experiments was 25°C , and the reaction number (*R.N*) is defined as:

$$R.N = \frac{T_m - T_i}{t} \quad ^{o}C/min \qquad (2)$$

Where T_m and T_i are the maximum and initial temperatures, respectively and t is the time in minutes taken to reach T_m .

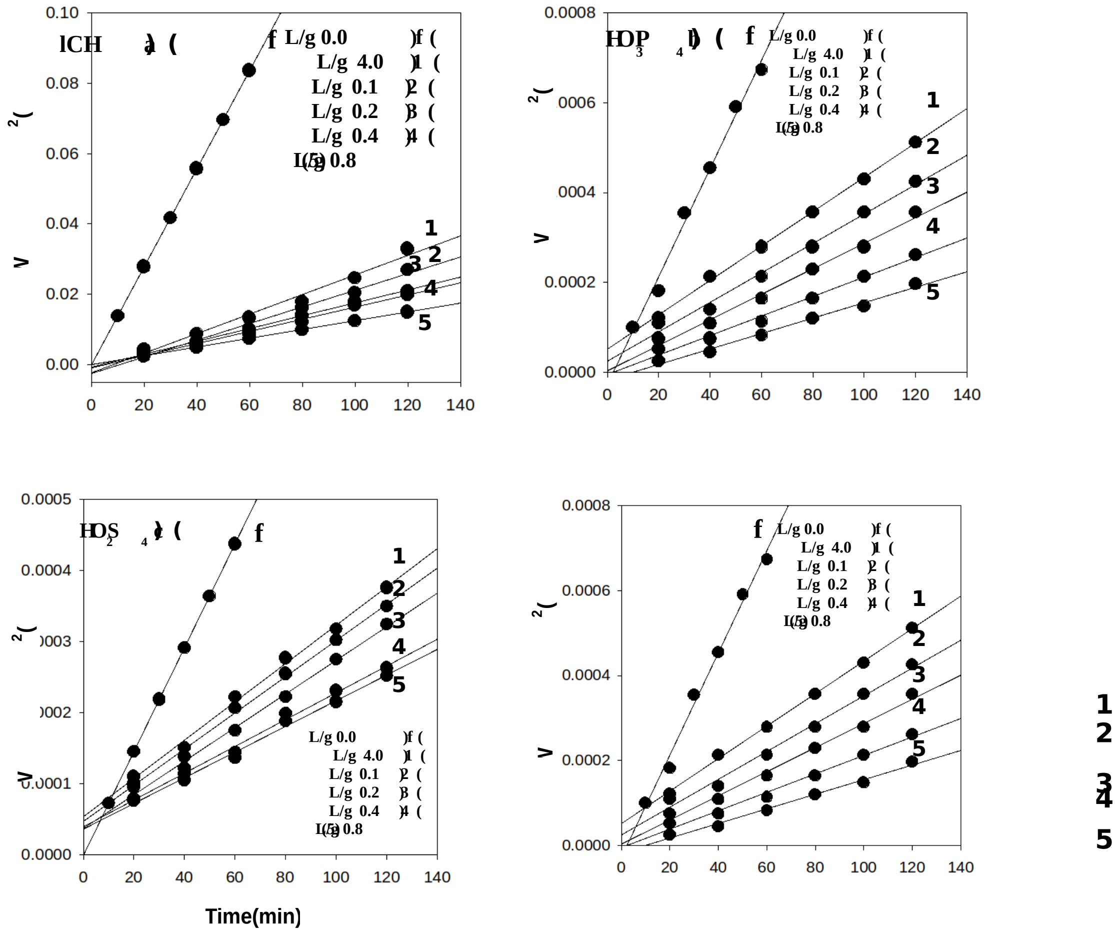
The potentiodynamic polarization measurements were carried out in a conventional three-compartment cell with a cylindrical rod of Al-Cu alloy as working electrode. A saturated calomel electrode (SCE) was used as reference and platinum wire as counter electrode. The measurements were performed after half an hour immersion with scan rate 2 m Vs^{-1}. All the measurements were performed in aerated solutions at room temperature (25±1 °C).

Results and discussion :

The corrosion rate, C.R., g/cm^2.min, for Al-Cu samples in aerated solutions of 2.0M of each of HCl, H_3PO_4, H_2SO_4 and 1.5M NaOH along a period of 120 min was constructed under weight-loss method. The calculated corrosion rates, C.R , are 1.39 e^{-3}, 8.20 e^{-6} , 3.64 e^{-6} and 5.21e^{-4} for 2.0M of HCl, H_3PO_4, H_2SO_4 and 1.5M NaOH, respectively .This indicates that the C.R. decreased in the order:

HCl < NaOH< H_3PO_4 < H_2SO_4

The effect of adding wide range (0.4 – 8.0 g/L) of the plant extract, ZSC on the weight-loss of Al-Cu samples in 2.0M of acids and 1.5M NaOH as corrosive media was represented by Figs.2(a,b,c,d) . As can be seen from the plots of this figure that in the presence of the extract the weight loss varies linearly with time, and it is lower than obtained in the free solution. These linear plots indicate the absence of insoluble surface film during corrosion, and the inhibitor was first adsorbed onto the metal surface and thereafter, inhibits the corrosion process [20]. Also it is obvious that the C.R decreases with increasing the concentration of the inhibitor. This indicates that the degree of inhibition depends upon the concentration of inhibitor and the nature of corrosive medium. The inhibition efficiency percent, IE% of the inhibitor in both acidic and alkaline media was calculated using the relationship (1).



Time(min)

Figs.2 (a, b, c, d): Weight loss-time curves for Al-Cu alloy in 2.0 M acidic and 1.5 M alkaline media in absence and presence of different concentrations of ZSC extract at 25°C.

The degree of the surface coverage θ which represents the part of the metal surface covered by inhibitor molecules was calculated using the following relationship [18]:

$$\theta = 1 - \left(\frac{R_{inh}}{R_{free}} \right) \qquad (3)$$

The values of C.R , IE% and θ for different concentrations of ZSC extract in 2.0M acidic and 1.5M alkaline media are listed in Table(2).

Table (2): Effect of ZSC extract concentration on C.R, IE% and θ for Al-cu alloy in . 2.0M acidic and 1.5M alkaline media at 25ºC

C_{inh} (g/L)	HCl			H_3PO_4			H_2SO_4			NaOH		
	C.R	%IE	Θ	C.R	%IE	Θ	C.R	%IE	Θ	C.R	%IE	Θ
0.4	2.78e-4	80.00	0.800	3.83e-6	53.29	0.533	2.69e-6	26.10	0.261	1.19e-4	70.40	0.704
1.0	2.37e-4	82.95	0.830	3.28e-6	60.00	0.600	2.54e-6	30.22	0.302	8.88e-5	77.91	0.779
2.0	1.82e-4	86.91	0.869	2.84e-6	65.37	0.654	2.36e-6	35.16	0.352	7.83e-5	80.52	0.805
4.0	1.74e-4	87.48	0.875	2.17e-6	73.54	0.735	1.88e-6	48.35	0.484	6.56e-5	83.68	0.837
8.0	1.24e-4	91.08	0.911	1.72e-6	79.02	0.790	1.80e-6	50.55	0.506	5.79e-5	85.60	0.856

Inspection of this Table revealed that as the plant extract concentration is increased, C.R decreases, while the IE% and θ increase, indicating the increase of the number of adsorbed molecules of ZSC extract on Al-Cu alloy surface. A good inhibition efficiency percent observed at 8.0 g/L with 91.08% and 85.60% in 2.0M HCl and 1.5M NaOH solutions, respectively. It is concluded that ZSC acts as an excellent inhibitor for corrosion of Al-Cu alloy in both media. The interaction between the inhibitor molecules and the metal surface can be provided by the adsorption isotherm. The Kinetic thermodynamic model [20] (El-Awady isotherm) has been found to give the best fit to the weight loss results of the inhibitor under test, by the following relation :

$$\log\left[\theta/(1-\theta)\right] = \log k` + y \log C \qquad (4)$$

Where $\log k`$ is the intercept of the straight line, and y is the number of inhibitor molecules occupying a given active site. The equilibrium constant of the adsorption process (K) is given by:

$$K = k`^{(1/y)} \qquad (5)$$

Values of $1/y$ <1 imply, the formation of multilayer's of the inhibitor molecules on the metal surface, while as $1/y$ >1 mean that a given inhibitor will occupy more than one active site [20] .

The equilibrium constant of the adsorption K is related to the free energy change of adsorption ΔG°_{ads} by the relation [(21)] :

$$K = \left(\frac{1}{55.5}\right)\exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (6)$$

Where 55.5 is the molar concentration of water, R is the gas constant and T is the absolute temperature. Fig. (3) Shows El-Awady adsorption isotherm for Al-Cu alloy in 2.0M acidic and 1.5M alkaline media in presence of ZSC extract. The parameters of y , $1/y$, K and ΔG°_{ads} are given in Table (3).

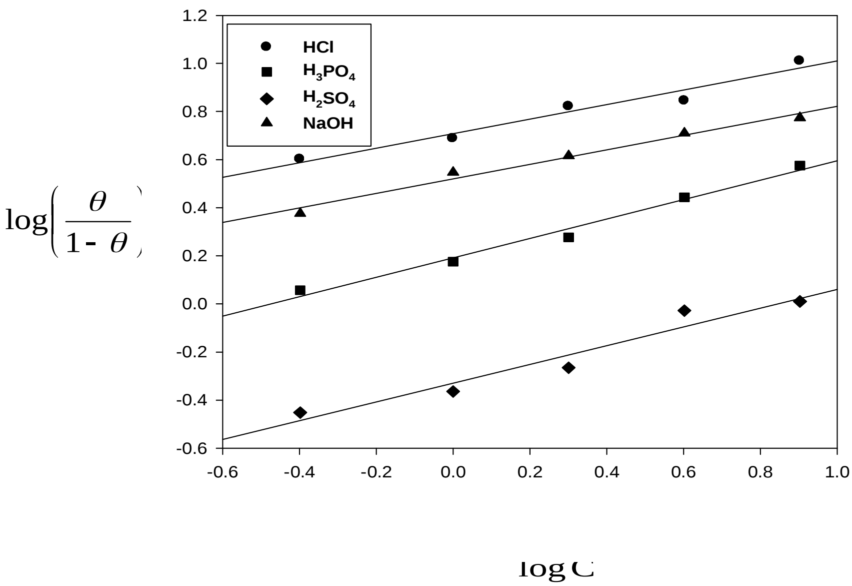


Fig. (3): El-Awady isotherm for Al-Cu alloy in 2.0 M acidic and 1.5 M alkaline media in .presence ZSC extract at 25ºC

Inspection of this Table, the values of $1/y$ indicated that the ZSC molecules will occupy more than one active site. The free energy change ΔG°_{ads} of adsorption of ZSC extract on alloy surface in 2.0M of acids found to be ranged from

-5.08 to -23.43 kJ/mol and 19.83 kJ/mol in 1.5M NaOH, respectively. It is well known that the values of ΔG°_{ads} less than -40 kJ/mol indicate a physisorption [22]. The calculated values of ΔG°_{ads} revealed the occurrence of a physical adsorption, and there is no chemical interaction between the inhibitor molecules and alloy surface. The negative sign indicating spontaneous interaction of inhibitor molecule with corroding metal surface [23].

Table (3): Linear fitting parameters and the standard free energy change of ZSC extract for Al-Cu alloy in 2.0M acidic and 1.5 M alkaline media at 25ºC .

Acids (M)	Kinetic-thermodynamic			
	Y	Y/1	K	G^{o}_{ads}(kJ/mol)Δ-
HCl	0.30	3.33	230.13	23.43
H_3PO_4	0.40	2.50	3.02	12.69
H_2SO_4	0.39	2.56	0.14	5.08
NaOH	0.30	3.33	53.82	19.83

The effect of temperature range (25-65ºC) on the corrosion rate C.R and inhibition efficiency IE% of Al-Cu alloy in both 2.0M HCl and 1.5 NaOH solutions in presence of 4.0 g/L of ZSC extract, was studied by weight loss method, and represented in Table (4). The data indicates that, C.R of Al-Cu alloy in absence and presence of the extract increases with increasing temperature. This is because an increase in temperature usually accelerates corrosion process, particularly in acid media in which H_2 gas evolution accompanies corrosion, giving rise to higher dissolution rate of metal. The values of IE% of the extract decrease with increasing temperature, and the high inhibition efficiency at 25ºC . The results suggest physical adsorption of ZSC extract on the Al-Cu alloy surface.

The apparent activati

The apparent activation parameters, E_a^{*} , ΔH^{*} and ΔS^{*} were obtained from Arrhenius equation[24] :

$$\log C.R. = \log A - \left(\frac{E_a^{*}}{2.303RT} \right) \tag{7}$$

And

Eyring equation[24]:

$$C.R. = \left[\left(\frac{RT}{Nh} \right) \exp\left(\frac{\Delta S^{*}}{R} \right) \right] \exp\left(\frac{-\Delta H^{*}}{RT} \right)$$

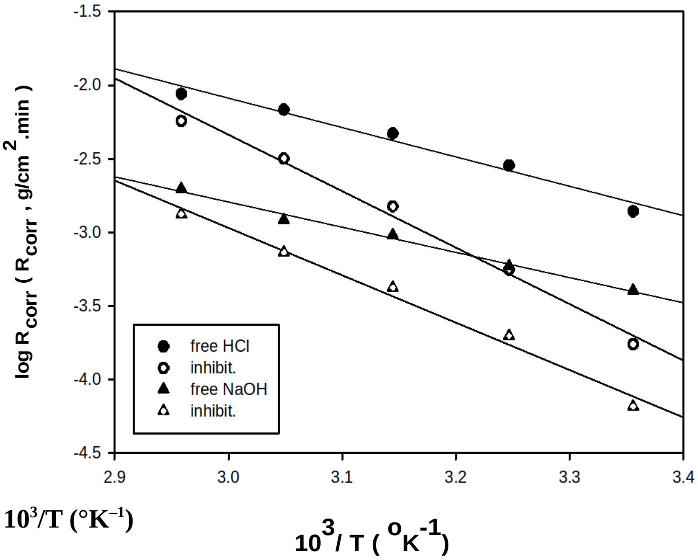
(8)

Fig.(4) represents Arrhenius plot of log C.R. versus $\frac{1}{T}$ for Al-Cu alloy in 2.0M HCl and 1.5M NaOH solutions and in presence of 4.0 g/L of ZSC extract. A straight lines were obtained with slope equal to $\left[\frac{-E_a^*}{2.303R}\right]$.

Table (4): Effect of temperatures on C.R and IE% for Al-Cu alloy in 2.0M acidic and 1.5 M alkaline media in absence and presence 4.0 g/L of ZSC extract.

	HCl				H_3PO_4				H_2SO_4				NaOH			
	C.R. $g/cm^2.min$		IE%		C.R. $g/cm^2.min$		IE%		C.R. $g/cm^2.min$		IE%		C.R. corr $g/cm^2.min$		IE%	
$C_{inh.}$ (g/L)	0.0	4.0	0.0	4.0	0.0	4.0	0.0	4.0	0.0	4.0	0.0	4.0	0.0	4.0	0.0	4.0
25 °C	1.39e-3	1.74e-4	-	87.48	8.20e-6	2.17e-6	-	73.54	3.64e-6	1.88e-6	-	48.35	4.02e-4	6.56e-5	-	83.68
35 °C	2.85e-3	5.58e-4	-	80.42	1.55e-5	5.64e-6	-	63.61	6.33e-6	3.53e-6	-	44.23	5.90e-4	1.98e-4	-	66.44
45 °C	4.70e-3	1.50e-3	-	68.09	2.00e-5	1.02e-5	-	49.00	8.00e-6	5.43e-6	-	32.13	9.58e-4	4.22e-4	-	55.95
55 °C	6.82e-3	3.18e-3	-	53.37	3.00e-5	2.00e-5	-	33.33	1.11e-5	8.65e-6	-	22.07	1.21e-3	7.31e-4	-	39.59
65 °C	8.73e-3	5.72e-3	-	34.48	3.80e-5	2.70e-5	-	28.95	1.55e-5	1.29e-5	-	16.77	1.98e-3	1.33e-3	-	32.83

Log R_{corr} ($R_{corr, g/cm^2 . min}$)

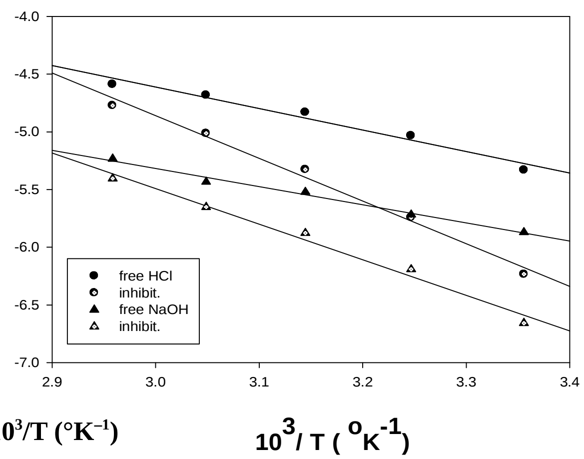


$10^3/T$ (°K^{-1})

Fig.)4(:Arrhenius plots of the corrosion rate for Al-Cu alloy in 2.0 M HCl and 1.5 M NaOH solutions in absence and presence of ZSC extract .

Also by plotting of $\log\frac{C.R.}{T}$ against $\frac{1}{T}$, gives straight lines with slope of $\left[\frac{-\ \Delta H^*}{2.303R}\right]$ and an intercept of $\left[\log\left(\frac{R}{Nh}\right)+\left(\frac{\Delta S^*}{2.303R}\right)\right]$ represented in Fig.(5 (.

Log R_{corr} ($R_{corr, g/cm^2 . min}$)



$10^3/T$ (°K^{-1})

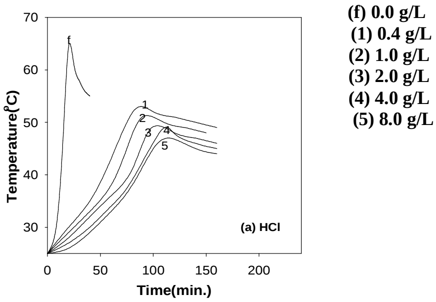
Fig.(5) : Eyring plots of the corrosion rate for Al-Cu alloy in 2.0 M HCl and 1.5 M NaOH solutions in absence and presence of ZSC extract .

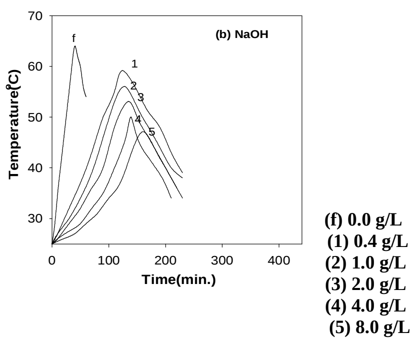
The values of activation parameters are listed in Table (5). It is demonstrated that, the of presence ZSC extract in both media increases the values of E_a^* comparing to its uninhibited, these attributed to an appreciable decrease in the adsorption process of the inhibitor on the alloy surface with increasing temperature, through a physical adsorption [25] . The higher ΔH^* value in presence of ZSC extract indicates that, the degree of the surface coverage decreases with increasing temperature, supporting the proposed physisorption mechanism. Also the negative values of ΔS^* mean, the increase in ordering accompanied the dissolution and inhibition processes.

Table (5): The values of activation parameters for Al-Cu alloy in 2.0 M acidic and .1.5 M alkaline media in the absence and presence of ZSC extract

Solutions (M)	free solutions			Inhibited solution		
	E_a^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	- ΔS^* J mol^{-1} $^oK^{-1}$	E_a^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	- ΔS^* J mol^{-1} $^oK^{-1}$
HCl	38.34	35.71	178.77	73.40	70.76	78.36
H_3PO_4	31.37	28.73	245.10	53.12	50.48	182.83
H_2SO_4	29.05	26.41	259.93	39.85	37.22	229.31
NaOH	32.71	30.07	209.19	61.63	58.99	125.76

The corrosion rate of Al-Cu alloy in 2.0M HCl and 1.5M NaOH solutions and in presence of different concentrations (0.4 - 8.0 g/L) of ZSC extract at 25ºC was studied using thermometric technique. Figs.6 (a, b) show that, all curves are characterized by slow rise in temperature with time and finally decrease after attaining a maximum value, T_m. The reaction number, R.N. of system which is evaluated by using the relationship (2).





Figs.6 (a,b): Thermometric curves for Al-Cu alloy in 2.0M HCl and 1.5 M NaOH . solutions in absence and presence of different concentrations of ZSC extract at T_i 25ºC

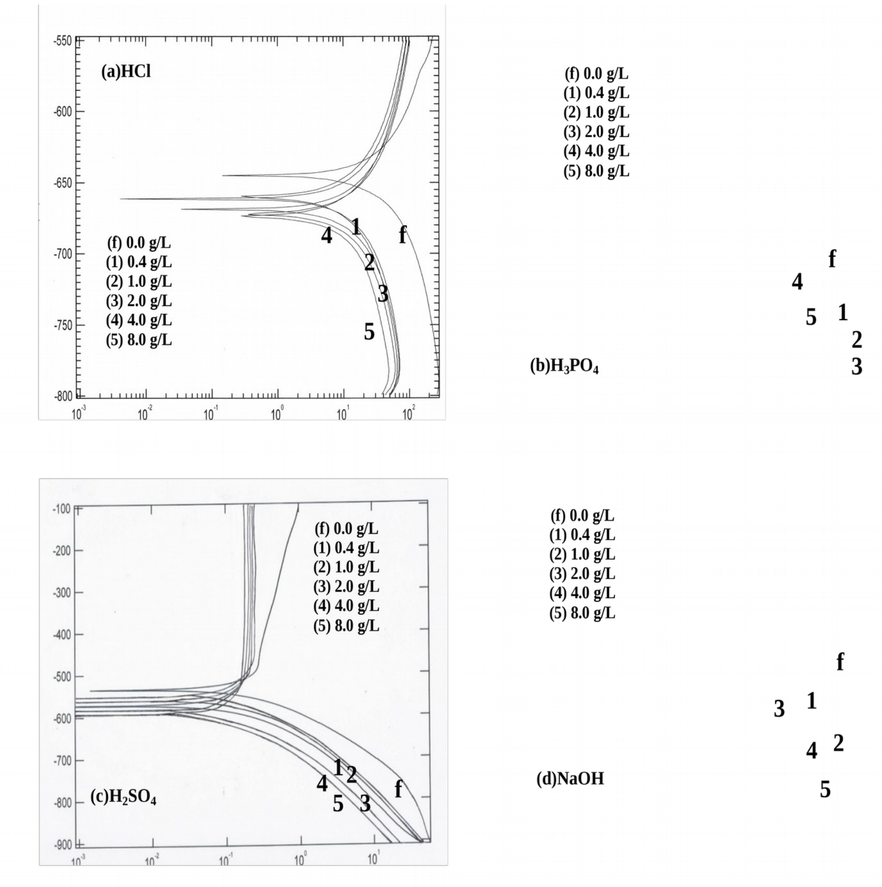
The maximum temperature, T_m measured in free 2.0M HCl is 64ºC and attained after 20 min, corresponds to the reaction number, R.N. of 1.95 ºC/min. While the dissolution in free 1.5M NaOH solution is somewhat slower, T_m is 64ºC but reached after 40 min, R.N. is 0.97 ºC/min. In presence of different concentrations of ZSC extract the T_m decreased and, the time required to reach T_m increased, these cause a large decrease in R.N. of system. This indicates that, the plant extract acts as inhibitor and adsorbs on both anodic and cathodic sites on the metal surface and provides the differentiating between strong and weak adsorption (26). The strong adsorption is noted in HCl than NaOH solution.

The inhibition efficiency percent, IE% is calculated by the relation:

$$IE\% = \left[1 - \left(\frac{R.N_{inh}}{R.N_{free}} \right) \right] \times 100 \qquad (9)$$

The calculated values of IE% of ZSC extract at 8.0 g/L are 90.36% and 85.85% in 2.0M HCl and 1.5M NaOH solutions, respectively, This results show that ZSC extract is a good inhibitor for Al-Cu alloy in both media , and this is in agreement to that obtained from the weight loss method.

Figs.7(a,b,c,d) show representative potentiodynamic polarization curves of Al-Cu alloy measured after reaching steady state potential, in aerated solutions of 2.0M HCl, H_3PO_4 , H_2SO_4 and 1.5M NaOH containing different concentrations (0.4 - 8.0 g/L) of ZSC plant extract. It is clear from the curves that the presence of ZSC extract in both media decreases the corrosion current (i_{corr}) and shifts the corrosion potential of alloy towards the negative direction due to the decrease in the rate of the cathodic reaction. This means that the cathodic reaction is inhibited to large extent than the anodic reaction. Since the transfer of the oxygen from the bulk solution to the Al-Cu alloy/solution interface will strongly affect the rate of oxygen reduction, and the adsorbed layer behaves as cathodic type inhibitor. The electrochemical parameters, E_{corr}, i_{corr} B_a, B_c are given in Table (6).



Figs.7 (a,b,c,d) :Potentiodynamic polarization curves for Al-Cu alloy in 2.0 M acidic and 1.5 M alkaline media in absence and presence of different concentrations of ZSC extract at 25ºC.

Table (6): Potentiodynamic parameters of Al-Cu alloy in 2.0 M acidic and 1.5 M alkaline media with different concentrations of ZSC extract at 25°C

	$C_{inh.}$ (g/L)	$-E_{corr}$ (mV)	i_{corr} (mA/cm^2)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	%IE
HCl	0.0	645.00	75.76	65.52	70.32	-
	0.4	661.21	12.67	60.21	65.21	83.28
	1.0	662.12	9.88	59.70	63.97	86.96
	2.0	669.02	8.54	57.21	60.12	88.73
	4.0	673.42	7.40	54.41	57.22	90.23
	8.0	674.51	6.48	50.79	52.59	91.45
H_3PO_4	0.0	535.61	2.96	130.89	99.95	-
	0.4	582.86	1.39	128.01	94.32	53.04
	1.0	588.21	1.22	129.62	96.15	58.78
	2.0	590.89	1.11	126.72	94.01	62.50
	4.0	594.12	0.96	126.55	95.71	67.57
	8.0	596.81	0.80	128.32	98.61	72.97
H_2SO_4	0.0	532.66	1.46	115.15	67.63	-
	0.4	554.42	1.09	111.72	60.12	25.34
	1.0	562.53	0.99	108.81	57.88	32.19
	2.0	573.29	0.94	105.91	58.93	35.62
	4.0	581.81	0.79	113.75	62.01	45.89
	8.0	592.65	0.72	112.42	64.32	50.68
NaOH	0.0	1299.89	30.00	155.01	145.25	-
	0.4	1414.55	8.91	134.74	134.54	70.30
	1.0	1414.55	7.98	132.96	132.89	73.40
	2.0	1432.66	6.80	121.77	135.51	77.33
	4.0	1450.78	5.80	128.76	128.83	80.67
	8.0	1465.27	4.38	133.70	129.27	85.40

The inhibition efficiency percent, IE%, at different concentrations of ZSC extract in both acidic and alkaline media was calculated from the corresponding electrochemical polarization measurements according to the following relation:

$$IE\% = 100 \times \left(1 - \frac{i_{corr(inh)}}{i_{corr}} \right) \qquad (10)$$

Where $i_{corr(inh)}$ and i_{corr} refer to the corrosion current densities in presence and absence of the inhibitor, respectively. The values of IE% in both media are also included in Table (6). Inspection of this Table reveals that, the values of the corrosion current density i_{corr} decreases with increasing the concentration of ZSC extract, indicating that the inhibitive property of the extract plant is concentration dependent. Tafel slopes B_a and B_c are more or less constant suggesting that, the inhibiting action of ZSC extract does not affect the mechanism of the corrosion process. Also the inhibition efficiency, IE% for ZSC extract in both media increases with increasing concentration, and at certain concentration (8.0 g/L), IE% reaches 91.45% and 85.40% in 2.0M HCl and 1.5M NaOH solutions, respectively. The results of the electrochemical measurement are in a good agreement with those of the chemical methods.

Conclusion:

Ziziphus Spina-Christi act as inhibitor, and the highest efficiency was observed at 8.0 g/L in 2.0M HCl and 1.5M NaOH solutions. Adsorption of ZSC extract on the surface of Al-Cu alloy in both media follows El –Awady isotherm. The calculated free energy change of adsorption of ZSC on Al alloy reveals a physical adsorption. The effect of temperature range (25-65ºC) reveals a physical adsorption of the inhibitor on the alloy surface. The potentiodynamic polarization measurements showed that, the extract was adsorbed mainly at cathodic sites, and acts as cathodic-type inhibitor. The chemical methods are in a good agreement with the potentiodynamic measurements; this improves the validity of the results obtained.

References:

1. Uhlig H.H. ; "Corrosion and Corrosion Control", John Wiley and Sons Inc. 2nd Ed. New York (1971)
2. Tomashov N.D.; "Theory of Corrosion and protection of Metals", Macmillan, p. 620 New York (1966).
3. Baccaria A.M.; Corros. Sci. 41, 885(1999)
4. Abdallah M.; Bull Electrochem. 16 (6), 258(2000)
5. Lochani M., Jeyaraj T., Raja C. and Ramyas. ; Electrochem. Sci. and Technol. 36(3-4) (2001)
6. Metikes – Hukovic M., Babic R. and Grubac Z.; J. Appl. Electrochem. 22(1), 35 (2002).
7. Al-Juhaiman L., Al-Mayouf A. and Suhaybany A.; J. Saudi Chem. Soc. 8(3), 547(2003).
8. Golgovici F., Branzoi F. and Branoi V. ; Mater. Chem. Phys. 78(1-3) (2004).
9. Ashassi – Sorkhabi H., Ghasemi Z. and Seifzadeh D.; Appl. Surf. Sci. 249(1-4), 408(2005).

10. Ahmed M. M. ; Portugalia Electrochimica Acta, 24, 1 (2006)
11. Avwiri G.O. and Igho F.O. ; Materials Letters, 57, 3705(2003).
12. Gunasekaran G. and Chauhan L.R.; Electrochim. Acta, 49, 4387 (2004).
13. Oguzie E.E. ; Mater. Chem. Phys. 99,441 (2006).
14. Oguzie E.E., Onuoha G.N. and Ejike E.N.; Pigment and Resin Technology, 36(1), 44(2007).
15. Abdel – Gaber A.M., Khamis E., Abo-Eldahab H. and Adeel S.H.; Mat. Chem. and Phys. 69,9 (2008).
16. Trease and Evans; Pharmacognosy, 15 Ed., New York, Toronto (2000).
17. Sanyal B. and Srrivastava K.; Br. Corros. J. 8, 28 (1975).
18. Sing R.N., Yerme N. and Singh W.R.; Corrosion , 45, 222(1989).
19. Mylius M. ; Z. Metallk , 14 , 233(1922)
20. El-Mahady G.A. and mahmoud S.S.; Corros. Sci. 51(6), 436(1995).
21. Donahue M., Nobe K. ; J. Electrochem. Soc. 112, 886 (1965).
22. Lipkowski J., Ross P.N. ; "Adsorption of Molecules at Metal Electrodes", New York (1992)
23. Bracher D. and Mercer A.D.; Br. Corros. J. 3, 120(1968).
24. Vashi R.T. and Champaneri V.A.; Ind. J. Chem. Techol. 4, 180(1997).
25. Sastri V.S. ; "Corrosion Inhibitors, Principle and Application", John Wiley and Sons, P. 33 New York (1998).
26. Aziz K. and Shams El-Din A.M.; Corros. Sci . 5(7) , 489(1965).