Effect of Soil Solution of Al Madina Al Monawara Area on the Corrosion of Aluminum in Acidic Media

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ABSTRACT The effect of Soil Solution of Al madina Al monawara Area (SSAA) on the corrosion inhibition of aluminum in 0.5M hydrochloric acid (HCl) was investigated by weight-loss experiments at 30 and 60°C and electrochemically at 30°C. The results indicate that SSAA acts as an inhibitor especially at low concentrations in HCl solution. It is found that, the percentage inhibition decreased with increasing the concentration of the inhibitor SSAA until 20%v/v, then it increases with increasing concentration. Potentiodynamic polarization curves indicated that the SSAA behaves as mixed type inhibitor. EIS measurements showed that the dissolution process occurs under activation control. At a concentration of 5%v/v, the percentage inhibition reached about 75.54% at 30°C and 43.16% at 60°C, respectively, and at 50%v/v the percentage inhibition equals 70.24% at 30°C and 52.75% at 60°C, respectively. The percentage inhibition decreased with the increase of temperature. The thermodynamic parameters for the adsorption of this inhibitor on the metal surface were calculated using the Freundlich adsorption isotherm and physical adsorption mechanism is proposed. SSAA was found to be an excellent potential corrosion inhibitor because of the high content of water, mineral salts such as silicon, aluminum silicate, magnesium silicate, carbonates, aldehydes, sulfides and different iron oxides.

Introduction:

The corrosion of metals in many industries, installations, constructions, and civil services such as sewage supplies, water and electricity is a serious problem. In order to minimize or prevent corrosion, inhibitors are usually used, especially in acidic solution systems. A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rate of a material, typically a metal or an alloy. Organic, inorganic, or a mixture of both inhibitors can inhibit corrosion by either chemisorption on the metal surface or reacting with metal ions and forming a barrier-type precipitate on its surface [1]. Because of the toxic nature and/or high cost of some chemicals currently in use as inhibitors, it is necessary to develop environmentally acceptable and inexpensive ones. Natural products can be considered as a good source for this purpose. The aqueous extracts from different parts of some plants such as Henna, *Lawsonia inermis* [1], *cordia latifolia* and curcumin [2], Rosmarinous officinalis L. [3], date palm, *phoenix dactylifera,* corn, henna, *lawsonia inermis,* corn, *Zea mays* [4], *Nypa Fruticans Wurmb* [5], and *Carica papaya* [6] have been found to be good corrosion inhibitors for many metals and alloys. Recently, an excellent researches about "natural products as corrosion inhibitors for metals in corrosive media" has been published [7-10].

 Aluminum was chosen in our studies since high temperature aggressive acids are widely used in industries, because aluminum and its alloys are very attractive

materials for engineering applications, and due to the lightweight and mechanical strength [8].

No study has been reported on the aqueous extract of *soil solution extract of Al madina Al monawara* area as corrosion inhibitor which is used in our present work, in terms of studying both the chemical and electrochemical effect and the temperature effect on the corrosion inhibition of aluminum in 0.5M HCl solution

The purpose of the present article is to study the application of *soil solution of Al madina Al monawara (SSAA) city*, as corrosion inhibitor for aluminum in aqueous solutions of hydrochloric acid (HCl).

The output of this study is intended to be a cheap and an eco-friendly natural source that can be utilized as a corrosion inhibitor for metals and alloys.

Experimental:

Material preparation

Pure aluminum metal (purity 98.5%) of the type AA 1060 obtained from Shabaan company was used for the investigation. All reagents used for the study were Analar grade and double distilled water was used for their preparation. Concentrations of HCl used was 0.5 M, while those of soil solution of *Al madina Al monawara* area (the inhibitor used) were 5, 10, 20, 30, 40 and 50%v/v [1]. Before each experiment, the electrodes were polished with different grade emery paper, degreased with acetone, rinsed under running water and finally dried with a stream of air.

Weight loss measurements

The apparatus and procedure followed for the weight loss measurements were as previously reported [11-15]. The tests were made in aerated solutions at room temperature 30 and 60°C using water bath. The difference between the weight at a given time and the initial weight of the electrode was taken as the weight loss which was used to compute the corrosion rate given by:

$$Corrosion \ rate = W/ At_\infty \quad\quad\quad (1)$$

where W is the weight loss (g), A the area of the specimen (cm^2), and t_∞ the exposure time (min.).

The percentage inhibition (I %) of aluminum was determined from weight losses as follows:

$$I\% = \frac{W_o - W_{in}}{W_o} \times 100\% \qquad (2)$$

where W_o and winh are the weight losses of aluminum specimens without and with inhibitor, respectively.

The surface coverage (Θ) was calculated from weight loss as follows:

$$\Theta = (W_o - \text{winh}) / W_o \qquad (3)$$

Weight loss measurements have been done at 30° C and 60° C.

Electrochemical measurements

Electrochemical measurements (impedence and polarization) were carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell with an ACM Gill AC instrument. The working electrode (WE) in the form of disc cut from aluminum has a geometric area of 0.7895 cm^2. A saturated calomel electrode (SCE) and a disc platinum electrode were used as reference and auxiliary electrodes, respectively. The temperature was thermostatically controlled at 30 ± 1 C. Details of the experimental procedure, electrolytic cell and electric circuits have been fully described [16-18].

The inhibition efficiencies from electrochemical methods (EIS and PDP), are respectively:

$$I_{Rct} \% = R_{cto}^{-1} - (R_{ct} / R_{cto}) \, x100 \qquad (4)$$

$$I_{Cdl} \% = (R_{Cdlo} - R_{Cdl}) / R_{Cdlo} \, x100 \qquad (5)$$

$$I_P \% = (I^{\circ}_{corr.} - I_{corr.}) / I^{\circ}_{corr.} \, x \, 100 \qquad (6)$$

where R^{-1}_{cto}, R_{Cdlo}, $I^{o}_{corr.}$, R^{-1}_{ct}, R_{Cdl} and $I_{corr.}$ are charge transfer, double layer capacitance and corrosion current without and with inhibitor, respectively.

Results and Discussion:

3.1. Analysis of Results from Weight Loss Method.

Table 1 shows the values of corrosion rates and inhibition efficiencies obtained from weight loss measurements of different concentrations of *SSAA* extract at 30 ℃. 5%v/v of the *SSAA* extract offered 75.54% corrosion inhibition efficiency to aluminum immersed in 0.5M HCl solution. When the concentration of *AASS* extract was increased, the inhibition efficiency decreased, and the corrosion rate increased until 20%, v/v, then the inhibition efficiency increased, and the corrosion rate decreased with increasing concentration of *SSAA*, this is due to the fact that when concentrations (10, 20)%v/v of *SSAA* extract are added, the protective film (Al^{3+}-*SSAA* complex) formed on the metal surface goes into the solution and thus destroying the protective film. It may be considered that the protective film formed may go into trans passive state, where the film is broken [19].

3.2. Analysis of Ac Impedance Spectra Curves.

AC impedance spectra have been used to detect the formation of the film on the metal surface. If the protective film is formed, the charge transfer resistance (R_{ct}) increases, and double layer capacitance (C_{dl}) value decreases [20]. The AC impedance spectra of aluminum immersed in various solutions are shown in Figure 1 (Nyquist plots). The AC impedance parameter, namely, charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are given in Table 2. When aluminum is immersed in aqueous solution containing HCl, the R_{ct} value is 35.55 ohm cm^2, and C_{dl} value is 2.484× 10^{-3} F/cm^2. When 5%v/v of *SSAA* extract is added, the R_{ct} value increases from 35.55 ohm cm^2 to 141.2 ohm cm^2, and C_{dl} value decreases from 2.484× 10^{-3} F/cm^2 to 0.308 × 10^{-3}. It suggests that a protective film is formed on the metal surface of the metal.

3.3. Analysis of Polarization Curves.

A polarization study has been used to detect the formation of protective film on the metal surface [21]. When a protective film is formed on the metal surface, the corrosion potential (E_{corr}) increases and the corrosion current (I_{corr}) decreases. The potentiodynamic polarization curves of aluminum immersed in various test solutions are shown in Figure 2. The corrosion parameters, namely, corrosion potential (E_{corr}) Tafel slopes (bc = cathodic; ba = anodic), and the corrosion current (I_{corr}) are given in Table 2 when aluminum is immersed in HCl solution. The corrosion potential of 0.5 M HCl is −620.2mV VS SCE. The formulation consisting of *SSAA* extract in presence of

HCl solution shifts the corrosion potential to more negative values. It is suggested that anodic reaction is controlled predominantly. It is clear that the anodic branches do not show any linearity due to the metal dissolution.

3.4. Inhibition Efficiency and Surface Coverage

The percentage of inhibition efficiency (I%) and surface coverage (Θ) were calculated using Eqs. (2&3) for different inhibitor concentrations and represented in Table 1 and Figure 3 at 30°C and 60°C, respectively. Inspection of data in Table 1 reveal that *SSAA* extract acts as inhibitor for corrosion of aluminum in hydrochloric acid solution. The results obtained reveal that I% and surface coverage increase as concentration of inhibitor increases at high concentrations (30-50%v/v) of *SSAA* extract but at low concentrations (5-20%v/v) I% and Θ decrease as concentration of inhibitor increases. The increase in inhibition efficiency and surface coverage as concentration of extract increases may be attributed to film formed on the metal surface due to complex chemical composition of extract, and the decrease in inhibition efficiency and surface coverage as concentration of extract increases may be attributed to the broken film formed on the surface of metal and go into trans passive state. The adsorbed species of *SSAA* extract mechanically screen coated part of aluminum surface from action of corrosive medium. This study revealed that *SSAA* extract showed higher inhibition efficiency and surface coverage at low concentrations when compared to values obtained at high concentrations.

The decrease in inhibition efficiency and surface coverage as recorded in Table 1 at 60°C may also be attributed to increase in average kinetic energy of components of extract which cause desorption of species of surface of aluminum sample. In view of this, increase in temperature may be associated with decrease in stability of adsorbed components- aluminum surface complex [22,23]. The results from Figure 3 indicate high inhibition efficiency at 30ºC when compared to values obtained at 60ºC. Similar observations have been reported earlier [24]. The significant difference between inhibition efficiency of extracts at 30°C and 60°C may be attributed to physical adsorption mechanism. In physical adsorption the forces of attraction are usually of weak Van der Waals type and this type of adsorption process can be easily reversed at high temperature, therefore inhibition efficiency decreases as temperature increases.

3.4. Adsorption Consideration

To determine the adsorption mode, various isotherms were tested and the Freundlich mode was found to be suitable for experimental findings Figure (4) findings given by [25]:

$$\Theta = K_{ads} \, C^n \qquad (7)$$

$$\log \Theta = \log K + n \log C \qquad (8)$$

where n is a constant, C is the inhibitor concentration and K_{ads} is the equilibrium constant of adsorption process.

The weight loss results were used to calculate the adsorption isotherm parameters at 30°C and 60°C. The plot of logΘ vs. logC for all investigated compounds gave a straight line (Figure 4) characteristic of the Freundlich adsorption isotherm. The equilibrium constant of adsorption of the extract of *SSAA* on surface of aluminum is related to free energy of adsorption $\Delta G°_{ads}$ according to Eq. (9) [26]:

$$\Delta G°_{ads} = - 2.303 R T \log (55.5K) \qquad (9)$$

where *R* is gas constant, T is temperature and K is equilibrium constant of adsorption, and 55.5 is concentration of water in solution. Generally, values of $\Delta G°_{ads}$ up to -20 kJ/mol or lower are consistent with electrostatic interaction between charged metal and charged molecules which signifies physical adsorption, while chemical adsorption values are more negative than -40kJ/mol or higher which involve charge sharing or transfer from the inhibitor molecules to metal surface to form coordinate type of bond [27,28].

The calculated $\Delta G°_{ads}$ values equal -14.31 kJ mol^{-1} at 30°C and -2.361 kJ mol^{-1} at 60°C are less negative than -20 kJmol^{-1}, therefore, that the adsorption mechanism of the investigated compounds on aluminum in 0.5 M HCl solution is typical of physisorption. The lower negative values of $\Delta G°_{ads}$ indicate that these inhibitors are not strongly adsorbed on the aluminum surface.

3.5. Effect of Temperature

The apparent activation energies (Ea) for the corrosion process in absence and presence of inhibitor can be evaluated from Arrhenius equation.

$$\log (CR_1 / CR_2) = E_a / 2.303 \, R \, \{1/T_1 - 1/T_2\} \qquad (10)$$

where CR_1 and CR_2 are corrosion rates at temperatures T_1 and T_2, respectively and *R* is gas constant. The heat of adsorption (Q_{ads}) can be obtained from the trend of surface coverage with temperature as follows using Eq. (11) [28]:

$$Q_{ads} = 2.303R[\log\{\Theta_2/(1-\Theta_2)\} - \log\{\Theta_1/(1-\Theta_1)\} \times \{T_1 x T_2/(T_2-T_1)\}]kJmol^{-1} \qquad (11)$$

while Θ_1 and Θ_2 are the degrees of surface coverage at temperatures T_1 and T_2.

The calculated values of E_a, and Q_{ads} of *SSAA* inhibitor using Eqs. 10 & 11 are shown in Table 4. The activation energy of *SSAA* extract ranges from 33.40 to 50.85 kJ/mol. The result shows that values of activation energy obtained in presence of inhibitor were higher than values obtained for blank, indicating that *SSAA* inhibited corrosion of aluminum in 0.5 M HCl. The heat of adsorption were all negative and range from -10.26 to -35.07 kJ mol^{-1}, indicating that adsorption of *SSAA* extract on aluminum surface is exothermic. The negative values also show that adsorption and hence inhibition efficiency decreases as temperature increases supporting the earlier proposed physisorption mechanism [27,29].

4. Conclusion:

The *soil solution of Al madinah Al monawarah (SSAA)* extract was found to be effective green inhibitor of aluminum corrosion in 0.5 M HCl. The corrosion process was inhibited by adsorption of the extract organic matter on the aluminum surface and the blocking of active sites. The extract of *SSAA* inhibited the corrosion of aluminum in acidic media by means of hindering both cathodic and anodic electrode processes, It is found that the inhibitive action of *SSAA* is basically controlled by temperature, and concentration of the inhibitor. This study also revealed that inhibition efficiency increases as concentration of inhibitor increases. The analysis indicates that inhibition efficiency and surface coverage decrease as temperature increases. The negative values of $\Delta G°_{ads}$ show that adsorption of inhibitor on the surface of aluminum sample is spontaneous. The adsorption behavior follows Freundlich isotherm which is based on physisorption phenomenon.
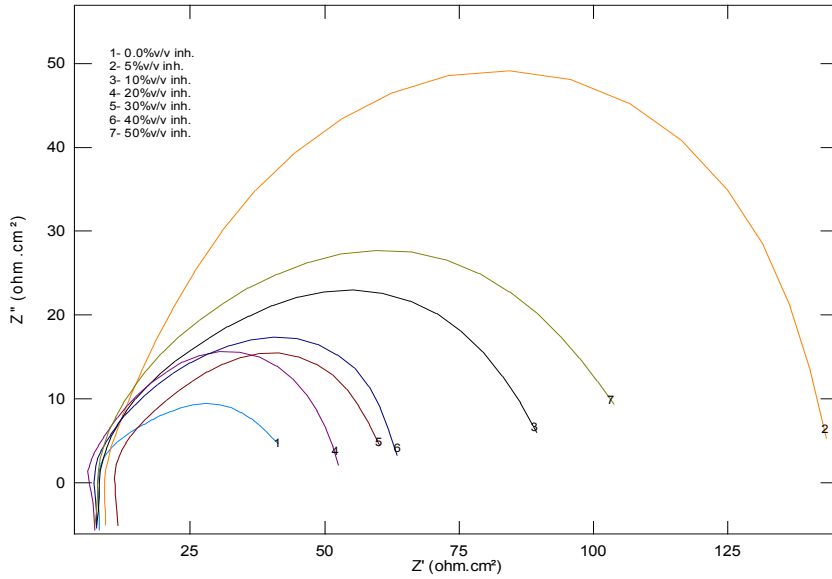
Fig. (1): Nyquist plots for aluminum corrosion in 0.5 M HCl in the absence and presence of inhibitor *SSAA* at 30°C.
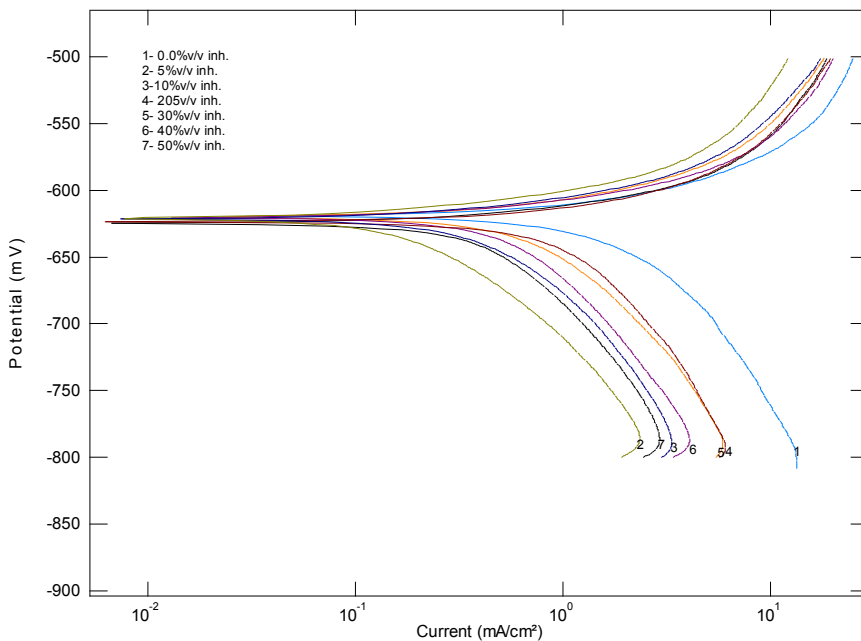

Fig. (2): Polarization curves for aluminum corrosion in 0.5 M HCl in the absence and presence of inhibitor *SSAA* at 30°C.
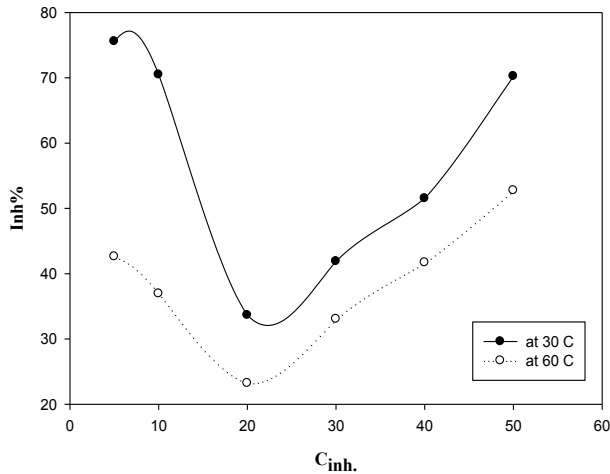
Fig.(3): Plot of Inh.% vs. $C_{inh.}$ for aluminum corrosion in 0.5 M HCl at 30°C and 60°C.
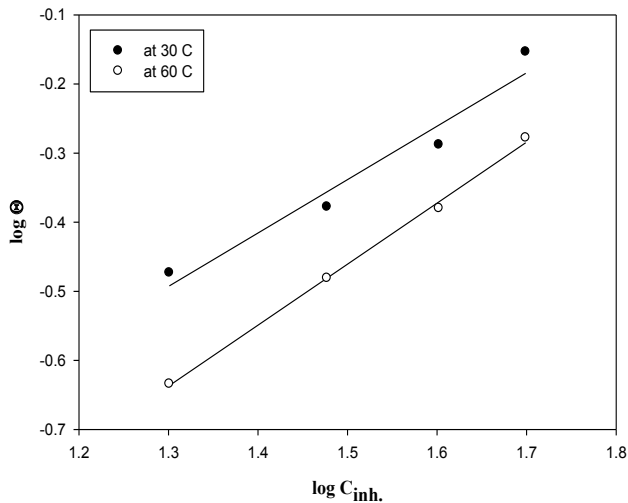

Fig. (4): Freundlich isotherm from weight loss method at temperatures 30˚C & 60˚C.

Table (1): Rates of corrosion and inhibition efficiency for aluminum corrosion in 0.5 M HCl in the absence and presence of *SSAA* from weight loss method.

C%v/v	30°C			60°C		
	$R' \times 10^5$ (g.cm-2.min.-1)	I%	Θ	$R' \times 10^5$ (g.cm-2.min.-1)	I%	Θ
0.0	1.3579	--	--	4.5732	--	--
5	0.3321	75.54	0.7554	2.5995	43.16	0.4316
10	0.4008	70.48	0.7048	2.8835	36.95	0.3695
20	0.9011	33.64	0.3364	3.5112	23.22	0.2322
30	0.7930	41.59	0.4159	3.0624	33.04	0.3304
40	0.6581	51.53	0.5153	2.6662	41.70	0.4170
50	0.4041	70.24	0.7024	2.1609	52.75	0.5175

Table (2): Electrochemical parameters and inhibition efficiency obtained from EIS and PDP measurements for aluminum corrosion in 0.5 M HCl in the absence and presence of *SSAA* at 30°C.

C%v/v	Impedance					Polarisation				
	$R_{sol.}$ (Ωcm^2)	R_{ct} (Ωcm^2)	C_{dl} (F) x 10^3	I_{Rct}%	I_{Cdl}%	$-E_{corr}$ (mV)	$I_{corr.}$ (mA/cm²)	b_a	b_c	I_{Icorr}%
0.0	9.820	35.55	2.484	--	--	620.2	2.7021	64.74	166.1	--
5	10.16	141.2	0.308	74.82	87.60	621.2	0.6193	37.62	113.1	77.08
10	9.496	86.75	0.954	60.35	61.59	622.0	0.7899	37.82	96.67	70.77
20	8.019	46.57	0.176	23.68	29.03	623.3	1.8158	52.47	89.86	32.80
30	12.69	52.01	1.507	31.65	39.33	619.8	1.5636	36.73	89.74	42.13
40	8.966	60.30	1.202	41.05	51.61	620.2	1.2217	39.20	95.97	54.79
50	9.134	102.3	0.703	64.53	71.71	625.1	0.7022	40.29	112.6	74.40

Table (3): Inhibition efficiencies for aluminum in o.5 M HCl in the presence of *SSAA* from ML at 30°C and 60°C and from EIS and PDP at 30°C.

C%v/v	I_{ML} % at 30°C	I_{ML}% at 60°C	I_{Rct} % at 30°C	I_{Cdl} % at 30°C	I_{PDP} % at 30°C
5	75.75	42.62	74.82	87.60	77.08
10	70.48	36.95	60.35	61.59	70.77
20	33.64	23.22	23.68	29.03	32.80
30	41.59	33.04	31.65	39.33	42.13
40	51.53	41.70	41.05	51.61	54.79
50	70.24	52.75	64.53	71.71	74.40

Table (4): Values of thermodynamic parameters for adsorption of extract of *SSAA* on surface of aluminum in 0.5 M HCl

Concentration of *SSAA (%v/v)*	Activation energy, E_a (kJ/mol)	Heat of adsorption Q_{ads}(kJ/mol)
0.0	30.01	-
5	50.85	-35.07
10	48.78	-39.28
20	33.63	-14.44
30	33.40	-10.26
40	34.59	-11.08
50	41.45	-22.06

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