J. Mater. Environ. Sci. 5 (2) (2014) 498-503 *Sultan et al.*
ISSN : 2028-2508
CODEN: JMESCN

Study of Some Natural Products as Eco – Friendly Corrosion Inhibitor for Mild Steel in 1.0 M HCl Solution

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Received 11 Sept 2013, Revised 5 Nov 2013, Accepted 5 Nov 2013
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Abstract

The effects of aqueous extract of Gummara of the Phoenix Dactylifera (AEGPD) and aqueous extract of Lactuca (AEL) on the corrosion inhibition of mild steel in 1M HCl solution were investigated by weight loss measurements at temperature range (30 – 60 °C). Results obtained showed that the percentage inhibition increases with the increasing of inhibitors concentration and decreases with the increasing of temperature. At a concentration of 2 g/L, the percentage inhibition reached about (93.82% and 95.81%) at 30 °C for (AEGPD) and (AEL); respectively. The thermodynamic functions of dissolution, activation energy and adsorption processes were calculated and discussed. Adsorption of the two inhibitors was found to follow the Langmuirs adsorption isotherm.

Keywords: Mild steel, Acid solution, Weight loss, Acid inhibition, Adsorption process, Corrosion inhibition.

Introduction

The studies of mild steel corrosion in acidic media receive more and more attention both of academics and industrials because of the wide applications such as acid pickling, industrial cleaning, acid descaling, oil well acid in oil recovery and the petrochemical processes. The electrochemical corrosion is generally caused by dissymmetry potentials between metal and strong acid. The aggressively of hydrogen ion is inevitable in uninhibited acid. H^+ and dissolved O_2 are named natural motors of corrosion [1–5]. Facing this problem, the corrosion inhibitors are required. Works on the inhibition are many so much so that we cannot quote them. But scientists are unanimous on the fact that this protection is provided by the adsorption of inhibitors on the metal surface. Then, compounds can adsorb on metal surface and block the active surface sites to reduce the corrosion rate. Many synthetic compounds offer good anticorrosion action; but most of them risk being highly toxic to both human beings and environment. In the later years, researchers reorient their studies to the used of naturally occurring substances. Plant extracts and oils have became important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention; therefore, finding naturally occurring substances as corrosion inhibitors is a subject of great practical significance [6–10].The objective of the present work was to study the inhibition effect of (AEGPD) and (AEL) as cheap, eco-friendly and naturally occurring substances on corrosion behaviour of mild steel in 1M HCl through weight loss measurements. The adsorption of these inhibitors was investigated and the thermodynamic adsorption parameters in absence and presence of these inhibitors were calculated and discussed.

Materials and methods

1. Materials and Solution

The materials used in the present study were mild steel coupons of rectangular shape in (59.6 × 20.7 × 6.7) cm size having composition 0.21% C, 0.05% Mn, 0.09% p, 0.05% S, 0.38% Si, 0.01% Al and the remainder iron containing a hole of about (3 mm) diameter near the upper edge was used for corrosion inhibitor study. The aggressive solutions of (1M HCl) were prepared by dilution of analytical grade 37% HCl with doubly distilled water.

2 Inhibitor Preparation

The natural products (Gummara of the Phoenix Dactylifera) and (Lactuca) used were collected from Abu – Al Khaseeb town, Basrah, Iraq. The extracts of these plants were obtained by dried the plants, and then finely powdered. 2g of dry powdered each plant were soaked in 60 ml distilled water at room temperature for 24 hours, and then filtered. The filtrate was added to an aqueous HCl solution to make 1.0 L stock solution in (1M HCl). From the stock solutions, a series of diluted solution in (1M HCl) were prepared with concentrations (0.2 g/L to 2 g/L).

3. Weight Loss Measurements

The mild steel coupons were ground and polished with emery paper up to 1200 grade, rinsed with distilled water, dried on a clean tissue paper, degreased by acetone for (5 sec) and dried by air at room temperature. After weighing accurately, the coupons were suspended vertically in a 100 ml beaker which contained (1M HCl) with and without the additives of different concentrations of an inhibitor. After (2 hours) immersion duration, the coupons were taken out, rinsed with doubly distilled water, washed with ethanol, dried and weighed according to ASTM (G1 – 71). Then the tests were repeated at different temperatures by using magnetic stirrer hot plates. In order to get good repeatability, experiments were carried out twice, and the average weight loss of two reading was reported.

Results and discussion

1. Effect of Inhibitor Concentration

The results of corrosion rate (W) (mg. cm^{-2}. h^{-1}) and the inhibition efficiency (%IE) and the degree of surface coverage (Θ) which obtained from the weight loss and by using the equations below, at different concentration of (AEGPD) and (AEL) in 1M HCl at 30 °C for 2h immersion.

$$\Theta = \frac{W_o - W_i}{W_o} \qquad \ldots(1)$$

$$\%IE = \Theta * 100 \qquad \ldots(2)$$

Where; W_O and W_i are the corrosion rates of mild steel in the absence and presence of the inhibitors; respectively.

The corrosion rate values of mild steel in 1M HCl containing inhibitor decreased as the concentration of the inhibitor increases, i.e. the corrosion inhibition enhances with inhibitor concentration, as shown in Fig. 1. This behaviour is the result of the fact that the adsorption amount and the surface coverage of inhibitor on mild steel increases with inhibitor concentration [11]. The (%IE) increased as the concentration of the inhibitor increases from (0.2 – 2 g/L) for the two additives. Also, the maximum (%IE) (93.82% and 95.81%) were obtained at the (2 g/L) and 30 °C, for (AEGPD) and (AEL); respectively as shown in Fig.2. The corrosion inhibition ability of the additives listed is greater for (AEL) than for (AEGPD) in 1M HCl.

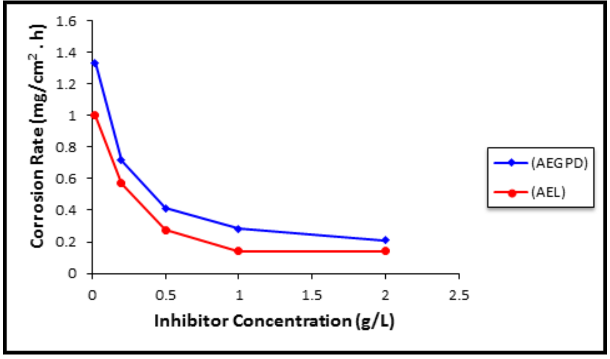

Figure 1: Variation of corrosion rates with concentrations of inhibitors in 1M HCl on mild steel surface at 30°C.

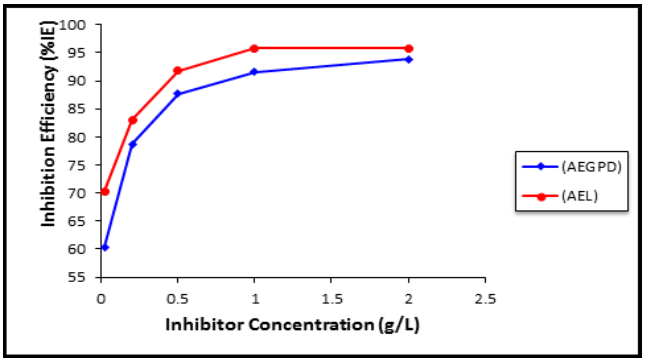

Figure 2: Variation of inhibition efficiency with concentrations of inhibitors in 1M HCl on mild steel surface

2. Adsorption Isotherm

The basic information of the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. Several attempts were made to fit various isotherms including Frumkin, Temkin, Frendlich, Bockriss, Flory – Huggins and Langmuir isotherms [12]. In the present study the results were best fitted by Langmuir adsorption isotherm. According to this isotherm, the surface coverage (Θ) is related to the inhibitor concentration (C) by [13, 14]:

$$\frac{\Theta}{1-\Theta} = K_{ads}.C \qquad \ldots(3)$$

Rearranging eq.(3) gives:

$$\frac{C}{\Theta} = \frac{1}{K_{ads}} + C \qquad \ldots(4)$$

A fitted straight line is obtained from the plots of C/Θ versus C with slopes close to 1, as seen in Fig. 3 (a & b) and the parameters are listed in Table 1. The strong correlation (R^2 >0.99) suggests that the adsorption of the inhibitor on mild steel surface obeyed the Langmuir adsorption isotherm. Table 1 also shows that the adsorption equilibrium constant (K_{ads}) value in (L/g) decreases with increasing temperature, which indicates that, it is easily and strongly adsorbed on the mild steel surface for the inhibitor at relatively lower temperature. But when the temperature was relatively higher, the adsorbed inhibitors tended to desorbs from the mild steel surface [15, 16]. Adsorption of (AEL) on mild steel surface is higher than (AEGPD).

Table 1: Adsorption parameters for (AEGPD) and (AEL) obtained from Langmuir isotherm at different temperatures.

Additives	Temperature °C	Adsorption parameters			
		R^2	Slope	Intercept	K_{ads} (L/g)
(AEGPD)	30	0.999	1.052	0.032	31.25
	40	0.985	1.041	0.168	5.952
	50	0.982	1.103	0.210	4.761
	60	0.972	1.174	0.258	3.875
(AEL)	30	0.999	1.032	0.020	50.00
	40	0.998	1.044	0.076	13.157
	50	0.996	1.100	0.102	9.803
	60	0.993	1.162	0.143	6.993

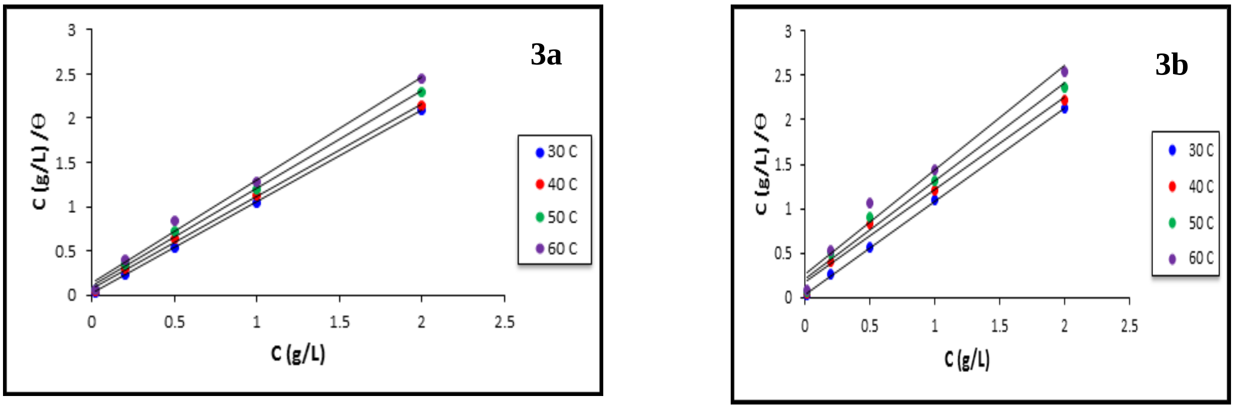

Figure 3(a, b): Langmuir adsorption isotherm model of (AEGPD) and (AEL) respectively in 1M HCl on mild steel surface at different temperatures.

3. Effect of Temperature on the Corrosion Inhibition of Mild Steel

From the corrosion studies of mild steel in 1M HCl in the absence of inhibitors at a temperature range of (30–60 °C) for 2 h immersion, it was found that the corrosion rate increased with increasing temperature, as shown in Fig. 4.

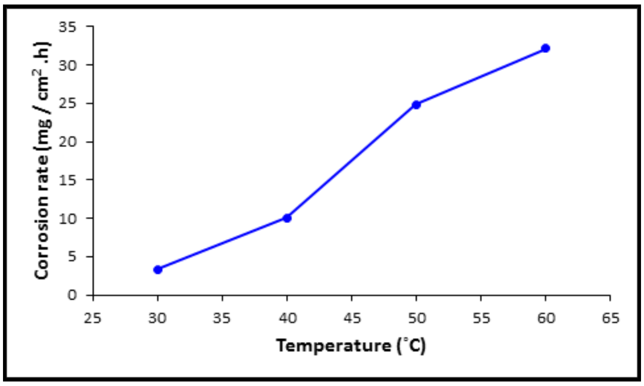

Figure 4: Variation of corrosion rate of mild steel in 1M HCl with temperature range (30 – 60 °C) for 2 h immersion.

The results obtained from temperature studies of the corrosion of mild steel in 1M HCl in the absence and presence of (AEGPD) and (AEL) at a temperature range of (30 – 60 °C) for 2 h immersion, revealed that increasing the temperature increases the corrosion rates and decreases the inhibition efficiency at all the concentrations studied. This is due to the desorption aided by increasing the temperature [17–19]. Thus, the behaviour proves that the adsorption of (AEGPD) and (AEL) on mild steel surface occurs through the physical adsorption. For the optimum concentration (2 g/L), the inhibition efficiency decreased from (93.82% to 78.44%) and from (95.81 to 81.67 %) with an increase in temperature from (30–60 ^{o}C), as shown in Fig. 5 for (AEGPD) and (AEL); respectively.

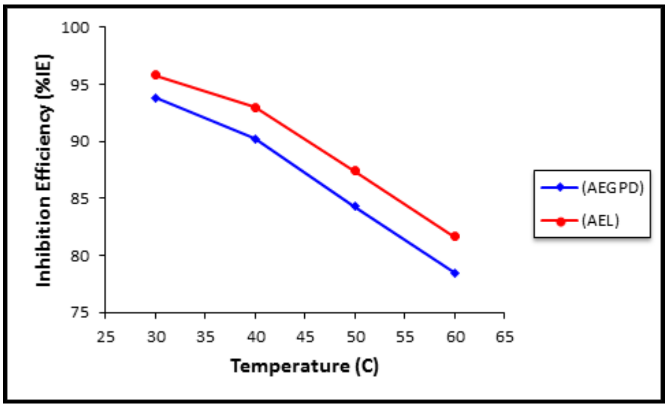

Figure 5: Variation of inhibition efficiency with the increase in the temperature on mild steel surface in 1M HCl at the optimum concentration of inhibitors (2 g/L) for 2 h immersion.

4. Thermodynamic Activation Functions of the Corrosion Process

The adsorption phenomenon has been successfully explained by thermodynamic parameter, to further elucidate the inhibition properties if inhibitor, the kinetic model was another useful tool to explain the mechanism of corrosion inhibition for the inhibitor. The activation parameters for the corrosion process were calculated from Arrhenius equation [29, 30]:

$$W = A \exp\left(-\frac{Ea}{RT}\right) \qquad \ldots(7)$$

Where; E_a represents the apparent activation energy, R the gas constant, A the pre – exponential factor and W is the corrosion rate, obtained from the weight loss method.

Arrhenius plots for the corrosion rate of mild steel were given in Figs (8 & 9). Values of E_a for mild steel in 1M HCl with (AEGPD) and (AEL) at different concentrations were calculated by linear regression between LnW and 1/T. results were shown in Table 3. An alternative formulation of Arrhenius equation is [31, 32]:

$$W = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^{\circ}}{R}\right) \exp\left(\frac{-\Delta H^{\circ}}{RT}\right) \qquad \ldots(8)$$

where; h is Plank s constant, N Avogadro s number, R the universal gas constant, ΔH°_{a} the enthalpy of the activation and ΔS°_{a} is the entropy of activation. Figs. (10&11) showed the plot of Ln (W/T) against 1/T.

Table 3: Activation parameters for the dissolution of mild steel in 1M HCl with different concentrations of (AEGPD) and (AEL).

Additives	Conc. (g/L)	E_a (kJ mol^{-1})	ΔH°_{a} (kJ mol^{-1})	ΔS°_{a} (kJmol^{-1}K^{-1})	$E_a - \Delta H^{\circ}_{a}$
Blank	0.0	64.300	61.689	-30.254	2.61
(AEGPD)	0.02	80.396	77.777	16.054	2.61
	0.2	93.258	90.655	54.215	2.61
	0.5	102.578	99.967	80.903	2.61
	1	99.410	96.799	65.938	2.61
	2	99.477	96.866	62.695	2.61
(AEL)	0.02	86.764	84.154	35.093	2.61
	0.2	93.973	91.362	53.966	2.61
	0.5	107.100	104.490	91.628	2.61
	1	109.553	106.951	94.122	2.61
	2	106.094	103.484	81.236	2.61

Straight lines were obtained with a slope of ($-\Delta H^{\circ}_{a}$ / R) and an intercept of $\mathrm{Ln}(R/Nh) + (\Delta S^{\circ}a/R)$ from which the values of ΔH°_{a} and ΔS°_{a} were calculated and listed in Table 3.From Table 3, it seemed that E_a and ΔH°_{a} varied in the same fashion. The values of E_a were higher for the inhibited solutions than that (64.300 kJ mol^{-1}) for the uninhibited solutions, and the values of E_a enhance with an increase in the inhibitor concentration from (0.02 to 2g/L) for both additives (the increase of E_a decelerated the corrosion rate of mild steel) [33].The positive values of ΔH°_{a} reflect that the endothermic nature of the mild steel dissolution process. The values of ΔS°_{a} were higher for inhibited solutions than that for uninhibited solutions. This suggested that an increase in randomness occurred on going from reactant to the activated complex [11, 33].

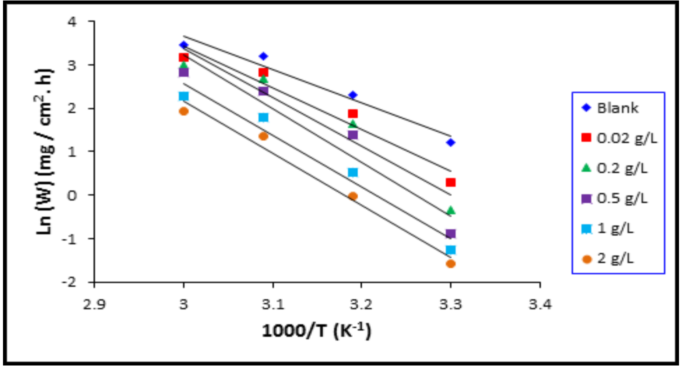

Figure 8: Arrhenius plots of LnW versus 1/T for mild steel in 1M HCl with (AEGPD) at different concentrations.

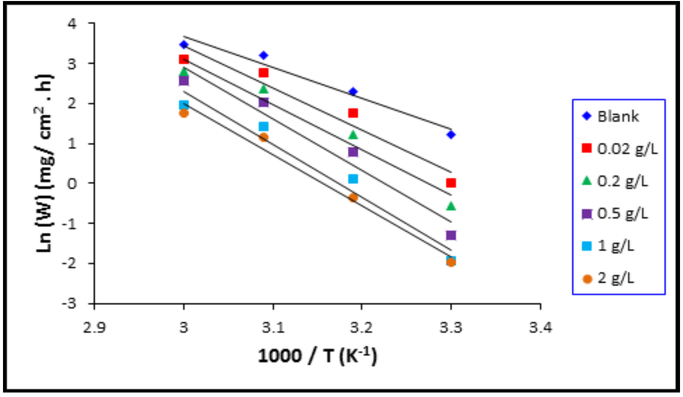

Figure 9: Arrhenius plots of Ln W versus 1/T for mild steel in 1M HCl with (AEL) at different concentrations.

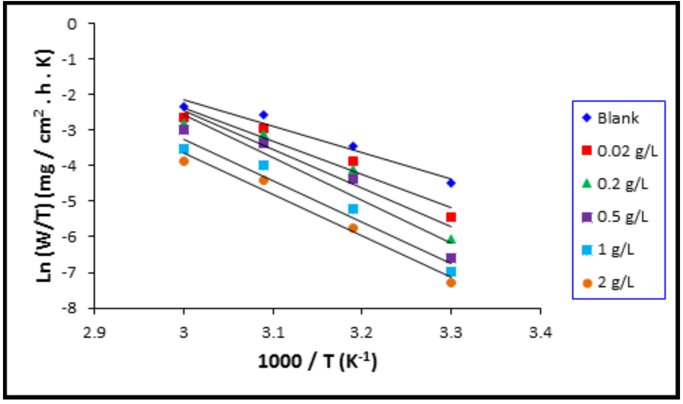

Figure 10: Arrhenius plots of Ln (W/T) versus 1/T for mild steel in 1M HCl with (AEGPD) at different concentrations.

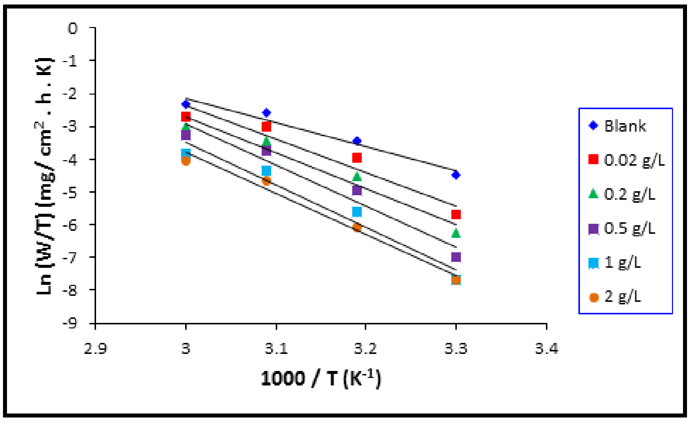

Figure 11: Arrhenius plots of Ln (W/T) versus 1/T for mild steel in 1M HCl with (AEL) at different concentrations.

Conclusions

The following conclusions can be drawn from this study:

1) The (AEGPD) and (AEL) were found to be a highly efficient inhibitor for mild steel in 1M HCl solution reaching about (93.82% and 95.81%) at 2g/L at 30°C, for (AEGPD) and (AEL); respectively.
2) The inhibition efficiency increases with increase in the concentration of these inhibitors and decreases with an increase in temperature.
3) The (AEGPD) and (AEL) are adsorptive inhibitors and their adsorption obeys the Langmuir's adsorption isotherm.
4) Thermodynamic adsorption parameters such as ΔG^o_{ads} , ΔH^o_{ads} and ΔS^o_{ads} , show that the inhibitors are adsorbed by a spontaneous exothermic process and a physisorption process can be suggested for the two inhibitors.
5) The (AEGPD) and (AEL) are an excellent, green, eco – friendly, and very cheap corrosion inhibitors for mild steel in 1M HCl solution, so it can be used to replace toxic and highly cost chemicals.

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