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Inhibition of aluminum corrosion using *Opuntia* extract

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Abstract

The inhibitive action of the mucilage extracted from the modified stems of prickly pears, toward acid corrosion of aluminum, is tested using weight loss, thermometry, hydrogen evolution and polarization techniques. It was found that the extract acts as a good corrosion inhibitor for aluminum corrosion in 2.0 M HCl solution. The inhibition action of the extract was discussed in view of Langmuir adsorption isotherm. It was found that the adsorption of the extract on aluminum surface is a spontaneous process. The inhibition efficiency (IE) increases as the extract concentration is increased. The effect of temperature on the IE was studied. It was found that the presence of extract increases the activation energy of the corrosion reaction. Moreover, the thermodynamic parameters of the adsorption process were calculated. It was found also that the *Opuntia* extract provides a good protection to aluminum against pitting corrosion in chloride ion containing solutions.

Keywords: A. Aluminum; Corrosion inhibition; Natural product; *Opuntia*

1. Introduction

It is well known that a compact, strongly adherent and continuous film is developed on aluminum upon exposure to the atmosphere or aqueous solutions. This film is responsible for the corrosion resistance of aluminum in most environments [1,2]. Nevertheless, in some cases, aluminum may be exposed to high concentrations of acids or bases. These solutions dissolve the passive film. In addition, aluminum may

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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. Consequently, several authors conducted a lot of work to find effective inhibitors for aluminum corrosion in different media [3–14]. The organic inhibitors establish their inhibition via the adsorption of their molecules on the metal surface forming a protective layer [3–6]. On the other hand, the inorganic inhibitors which are mainly oxidizing agents such as chromates act as anodic inhibitors and their metallic atoms are enclosed in the film improving its corrosion resistance [7–11]. Most of investigated compounds are toxic and cause severe environmental hazards. Recently, good results were obtained when lanthanide salts, which have a low toxicity, were employed as aluminum corrosion inhibitors [12–14]. Unfortunately, these compounds are very expensive.

Our previous work [15] reported a successful use of vanillin as corrosion inhibitor for aluminum in high acidic solution. The present work is another trial to find a cheap and environmentally safe inhibitor for aluminum corrosion in the acidic solution, where the aqueous extract of *Opuntia* plant stem is tested. This plant belongs to the family Cactaceae and has the scientific name (*Opuntia ficus* Mill). Weight loss measurements, thermometry, gasometry and potentiostatic polarization techniques are used, in the present work, to calculate the inibition efficiency of the *Opuntia* extract. The effect of temperature on the corrosion reaction rate in free and inhibited acid solutions was also investigated. Moreover, the ability of the extract to provide a protection against pitting corrosion of aluminum in chloride ion containing solutions was studied using potentiodynamic polarization.

2. Experimental methods

Pure aluminum provided by the "Aluminum Company of Egypt, Nagh ammady" was used. Coupons with surface area of 1.0 cm^2 were used for weight loss, thermometry and hydrogen evolution measurements. For potentiostatic studies, a cylindrical rod embedded in araldite with exposed surface area of 0.6 cm^2, was used. The electrodes were polished with different grades of emery papers, degreased with acetone and rinsed by distilled water.

Weight loss measurements were carried out as described elsewhere [16]. Potentiostatic polarization studies were carried out using EG&G model 173 Potentiostat/Galvanostat. Three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. For potentiodynamic experiments, the working aluminum electrode was held at the potential of hydrogen evolution for 10 min before the potential sweep starts, to get rid of any pre-immersion oxide film may present on the surface. The inhibition efficiency (IE) was calculated using the following equation:

$$\mathrm{IE} = [(I - I_\mathrm{i})/I] \times 100$$

where I and I_i are the corrosion rates in free and inhibited acid, respectively.

The reaction vessel used in thermometry experiments was basically the same as described by Mylius [17]. The thermometric experiments were carried out as described elsewhere [15]. The variation in temperature of the system is measured to ±0.5 °C as a function of time. The reaction number (RN) is defined as:

$$\mathrm{RN} = (T_\mathrm{m} - T_\mathrm{i})/t\ ^\circ\mathrm{C\,min}^{-1}$$

where T_m and T_i are the maximum and initial temperatures, respectively and t is the time in minutes elapsed to reach T_m. IE is calculated as the percent reduction in the RN:

$$\mathrm{IE} = [(\mathrm{RN}_\mathrm{f} - \mathrm{RN}_\mathrm{i})/\mathrm{RN}_\mathrm{f}] \times 100$$

where (RN_f) and (RN_i) are the RNs of aluminum dissolution in free acid and in presence of inhibitor, respectively.

The reaction vessel used for hydrogen evolution and the procedure of determination of dissolution rate of aluminum in acid solution were the same as described elsewhere [18]. All chemicals used for preparing the test solutions were of analytical grade and the experiments were carried out at room temperature, 30 ± 1 °C.

The flat stem of *Opuntia* was washed thoroughly with distilled water and its green cover was removed, then it was divided into small pieces and squeezed between two rotating rolls. The extract was then filtered and used directly in the experiments. Both the freshly prepared extract and that aged for one month give almost the same results.

3. Results and discussion

3.1. Weight loss measurements

Fig. 1 represents the relation between time and weight losses of aluminum coupons in solutions of 2.0 M HCl devoid of and containing different concentrations of *Opuntia* extract. Inspection of the figure reveals that the loss of weight increases linearly with increasing time in all tested solutions. However, the slopes of the obtained lines, which represent the rates of weight loss, are affected by addition of *Opuntia* extract. The presence of the extract causes a sharp decrease in the rate of weight loss. IEs at different concentrations of the extract were calculated using the following equation:

$$\mathrm{IE} = [(r - r_\mathrm{i})/R] \times 100$$

where r and r_i are the rates of corrosion of free and inhibited acid solutions, respectively. The values of IEs of different *Opuntia* extract concentrations are given in Table 1. The tabulated data reveal that, the *Opuntia* extract acts as a good corrosion inhibitor for the acid corrosion of aluminum. The corrosion inhibition increases with increasing extract concentration.

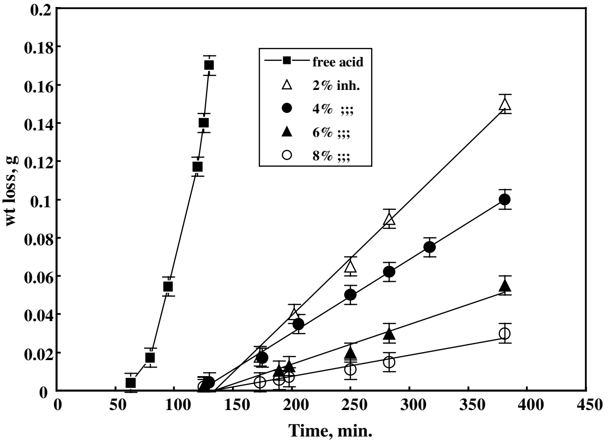

Fig. 1. Weight loss during corrosion of aluminum in free and inhibited acid solutions.

Table 1
IE and θ of different concentrations of *Opuntia* extract for aluminum corrosion in 2 M HCl solution as obtained from weight loss measurements

Concentration (v%)	IE%	θ
2	76	0.76
4	87	0.87
6	93	0.93
8	96	0.96

The *Opuntia* extract contains mainly polysaccharide which is a mixture of mucilage and pectin [19,20]. The mucilage, extracted from cladodes (modified stems), contains residues of D-galactose, D-xylose, L-rhamnose, L-arabinose and D-galacturonic acid [21,22]. The mucilage has a uronic content of about 10% and molecular weight of 4.3×10^6 [23]. In addition to mucilage (acidic fraction), the stems contain neutral carbohydrate-containing polymers consisting of two glucans and a glycoprotein [24]. It also contains at least seven non-volatile acids including malic and citric acids [25]. The adsorption of these compounds on the electrode surface makes a barrier for mass and charge transfers. This situation leads to a protection of the metal surface from the attack of the aggressive anions of the acid. The degree of protection increases with increasing of the surface fraction occupied by the adsorbed molecules. As the extract concentration is increased, the number of the adsorbed molecules on the surface increases. A parameter (θ), which estimated from the IE values, could be used to represent the fraction of the surface occupied by the adsorbed molecules. The values of this parameter for different extract concentrations are given in Table 1.

Inspection of Table 1 reveals that the value of θ increases with increasing inhibitor concentration. The dependence of the fraction of the surface occupied by the adsorbed molecules on the inhibitor concentration (C) is illustrated in Fig. 2. A plot of C/θ versus C gives a straight line with unit slope. This result suggests that the ad-

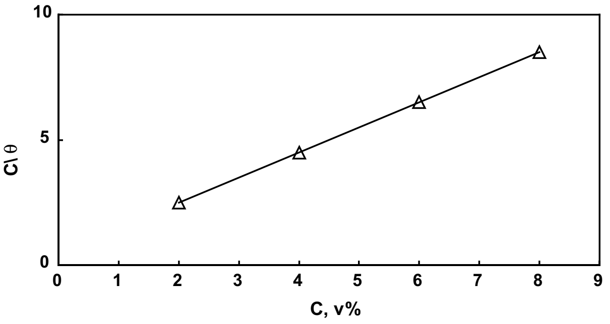

Fig. 2. Relationship between C/θ and inhibitor concentration.

sorption of inhibitor molecules on the aluminum surface follow Langmuir isotherm. Thus, this result suggests that there are no interaction or repulsion forces between the adsorbed molecules. It is of interest to mention here that, the θ values obtained from the other used techniques obey also the Langmuir adsorption isotherm.

3.2. Thermometry

Fig. 3 represents the change of temperature due to the corrosion reaction of aluminum in solutions of 2 M HCl devoid of and containing different concentrations of *Opuntia* extract. An interesting behavior could be observed in the figure where the temperature of the corroding systems decreases below the room temperature upon immersion of the aluminum sheet in the test solution. The temperature continues to decrease until it acquires a certain value after a certain time, and then it starts to increase again. It is of interest to note that, the extent of decrease in temperature value and the corresponding time depend on the solution composition. Thus, the temperature depression is the smallest within a shortest time in case of free acid solution. On the other hand, both the temperature depression and its corresponding time increase with increasing inhibitor concentration. It is of interest to mention here

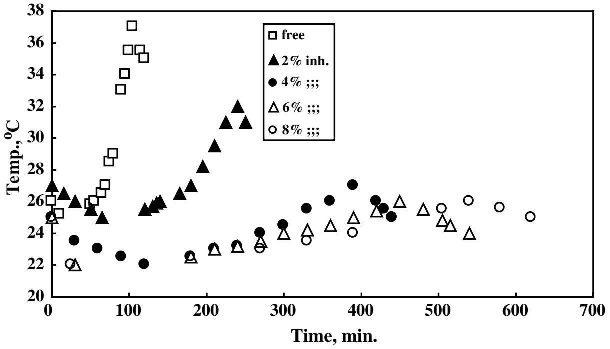

Fig. 3. Thermometric curves of aluminum in free and inhibited acid solutions.

Table 2
Effect of *Opuntia* extract concentration on its IE for aluminum corrosion in 2 M HCl solution as revealed from thermometry technique

Extract concentration (v%)	IE%
2	67.7
4	83.8
6	92.7
8	94.3

that, this phenomenon did not recorded in the previous work [15] on corrosion of aluminum in 5 M HCl solution. So, for testing the reproducibility of this phenomenon, different concentrations of HCl ranging between 0.5 and 6.0 M were used in the thermometry test. It was found that the temperature depression and its time decrease with the increase of acid concentration up to 4 M where the depression is completely disappeared. This temperature depression could be interpreted in view of the endothermic nature of the reaction between the pre-immersion aluminum oxide film and the acid according to the equation: $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ AH = +98.65 Kcal/mol. The enthalpy value of the above reaction is calculated using the standard enthalpies of formation of the participant compounds [26].

After the consumption of the pre-immersion oxide film, the temperature of the system starts to rise due to the exothermic corrosion reaction. In the free acid, the temperature reached a maximum value (T_m) of 35 °C within 120 min. the initial temperature was taken as the minimum temperature acquired by system after the complete removal of the pre-immersion oxide film. Inspection of Fig. 3 reveals also that the addition of *Opuntia* extract leads to decreasing the maximum temperature and increasing the time required to reach it. This behavior reflects the high IE of the extract toward aluminum corrosion in HCl medium. The IE increases as the addition concentration is increased. Table 2 represents the values of IEs for different additive concentrations calculated using thermometry technique.

Further inspection of Fig. 3 reveals that the temperatures of all systems decreased again after reaching their maximum values. This behavior could be explained in view of decreasing of the acid concentration with increasing reaction time. Thus, the corrosion rate decreases in turn, and the quantity of the evolved heat is also decreased.

3.3. Hydrogen evolution measurements

The volume of hydrogen evolved during the corrosion reaction of aluminum in 2 M HCl solutions devoid of and containing different concentrations of *Opuntia* extract is measured as a function of the reaction time, and the data are represented graphically in Fig. 4. Inspection of the figure reveals that, the hydrogen evolution starts after a certain time from the immersion aluminum coupon in the test solution. It may be expected that this time correspond the period needed by the acid to destruct the pre-immersion oxide film, and is known as the incubation period. In contrast to thermometry technique, hydrogen evolution experiments do not reveal a clear relation between the incubation period and solution composition.

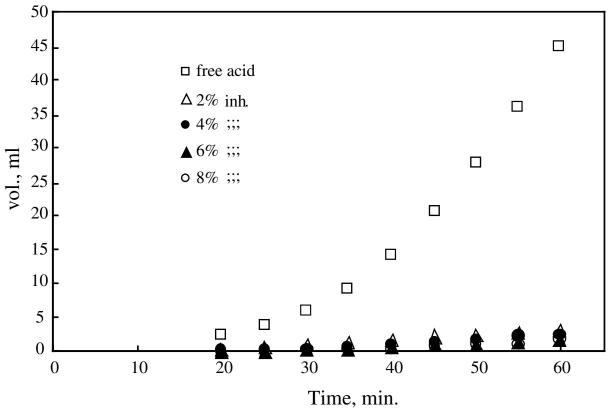

Fig. 4. Hydrogen evolution during corrosion of aluminum in free and inhibited acid.

Table 3

IE for different concentrations of *Opuntia* extract toward aluminum corrosion in 2 M HCl solutions, as revealed from hydrogen evolution experiments

Extract concentration (v%)	IE%
2	93.6
4	94.4
6	96.5
8	97.07

Further inspection of Fig. 4 reveals linear relationship between the time of reaction and the volume of hydrogen evolved, in all of the tested solutions. However, the presence of the extract decreases, markedly, the slope of the straight line. Since the slope of the line represents the corrosion reaction rate, it could be concluded that the *Opuntia* extract has an excellent ability to inhibit the corrosion of aluminum in the acid solution. The values of IEs of different concentrations of the extract are given in Table 3.

Inspection of Table 3 reveals that the IE increases as the concentration of the extract is increased. It is of interest to note that the values of IEs of low concentrations are far from those calculated by weight loss and thermometry techniques. On the other hand, the IEs of the high concentrations are comparable for the three techniques.

3.4. Potentiostatic polarization

Anodic and cathodic polarization curves, of aluminum in 2.0 M HCl solutions devoid of and containing different concentrations of *Opuntia* extract, are traced at 5 mV/s. The electrochemical parameters; corrosion potential (E_{corr}), corrosion rate (I_{corr}), anodic Tafel constant (β_a), cathodic Tafel constant (β_c) and IE were calculated and given in Table 4.

Table 4
Electrochemical parameters of aluminum corrosion in free and inhibited HCl solutions

Extract concentration (v%)	E_{corr} (mV)	I_{corr} (μA/cm^2)	IE%	β_a (mV/decade)	$-\beta_c$ (mV/decade)
–	−888	39.96	–	216	393
2	−819	13.6	65.9	78	241
4	−815	10.8	72.9	73	202
6	−812	8.16	79.5	58	187
8	−812	5.83	85.4	42	168

Inspection of Table 4 reveals that the corrosion potential shifts to less negative values upon addition of the inhibitor. Nevertheless, the corrosion potential is almost independent on the inhibitor concentration. On the other hand, the addition of *Opuntia* extract decreases markedly the corrosion current. This behavior reflects its ability to inhibit the corrosion of aluminum in HCl solution. The IE increases as the extract concentration is increased. Further inspection of Table 4 reveals also that both the anodic and cathodic Tafel constants decrease upon addition of inhibitor and decrease further with increasing inhibitor concentration. This behavior suggests that the extract inhibits the corrosion of aluminum via the adsorption of its molecules on both anodic and cathodic sites and consequently, it acts as mixed inhibitor.

It is important to note that the IEs calculated using polarization method are smaller than the values obtained by the other methods. However, four methods were used in the present work to determine the inhibitive action of *Opuntia* extract toward corrosion of aluminum in HCl solution. If the techniques which give the highest and the lowest values are excluded, we still have the proof of the excellent inhibitive power of the *Opuntia* extract.

3.5. Effect of temperature

The effect of temperature on the corrosion rate of aluminum in free acid and in presence of 4% inhibitor was studied in the temperature range of 30–70 °C, using weight loss measurements. It was found that the rates of aluminum corrosion, in free and inhibited acid solutions, increase with increasing temperature. The aluminum corrosion rate in inhibited solution is affected by the rise of temperature more than that in free acid solution. Consequently, the IE of the extract decreases with increasing temperature. This result suggests a physical adsorption of the extract compounds on the aluminum surface. The plot of logarithm of the corrosion rate versus the reciprocal of absolute temperature gives straight lines (Fig. 5) according to Arrhenius equation: $\ln r = A - E_a/RT$ where r is the corrosion rate, A is the constant frequency factor and E_a is the apparent activation energy. The values of E_a were calculated and found to be 38.49 and 64.43 $\mathrm{kJ\,mol^{-1}}$ for corrosion reactions in free and inhibited acid, respectively. It is clear that, the activation energy increases in presence of *Opuntia* extract and consequently the rate of corrosion reaction is decreased.

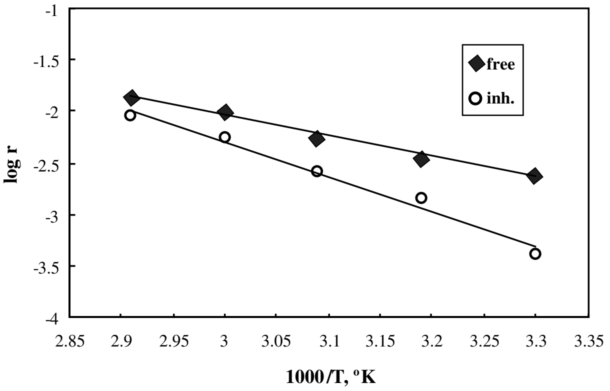

Fig. 5. Effect of temperature on aluminum corrosion rate in free and inhibited acid.

It has been mentioned before, in the weight loss experiments, that the adsorption of the extract on the metal surface follows Langmuir adsorption isotherm. However, the Langmuir adsorption isotherm may be written in the form [27]:

$$\log C = \log[\theta/1 - \theta] - \log k$$

where $\log k = -1.74[\Delta G^0/2.303RT]$.

Thus, by using these equations, we can calculate the standard free energy of adsorption ΔG^0. On the other hand, the enthalpy of adsorption ΔH^0 as well as entropy of adsorption ΔS^0 can be calculated using the following equations [28]:

$$\Delta H^0 = E_a - RT \quad \text{and} \quad \Delta G^0 = \Delta H^0 - T\Delta S^0$$

The calculated values of the thermodynamic parameters, ΔG^0, ΔH^0 and ΔS^0 at 30 °C, for the acid solution contains 4% of extract, were found to be −11.29, −2497 and −8.2 kJ mol^{-1}, respectively. The negative sign of the thermodynamic parameters indicates that the adsorption process is spontaneous, exothermic and increases of the system order.

3.6. Pitting corrosion

Potentiodynamic curves of aluminum electrode were traced in solutions of 3.5% NaCl devoid of and containing different concentrations of *Opuntia* extract. The aluminum potential was swept from hydrogen evolution potential toward anodic direction up to the pitting potential, at scanning rate of 1.0 mV/s. No anodic oxidation peaks or any fine structures could be observed in the anodic scan. The pitting potential was taken as the potential at which the current increases sharply to a very high value. The pitting potential values are given in Table 5. Inspection of the data of the table reveals that the presence of *Opuntia* extract shifts the pitting potential of aluminum to less negative potential. This result suggests that the extract acts as pitting corrosion inhibitor for aluminum.

Table 5
Values of pitting potential E_{pit} of aluminum in free and inhibited 3.5% NaCl solutions

Inhibitor concentration (v%)	0	2	4	6	8
E_{pit} (mV)	−752	−731	−710	−663	−636

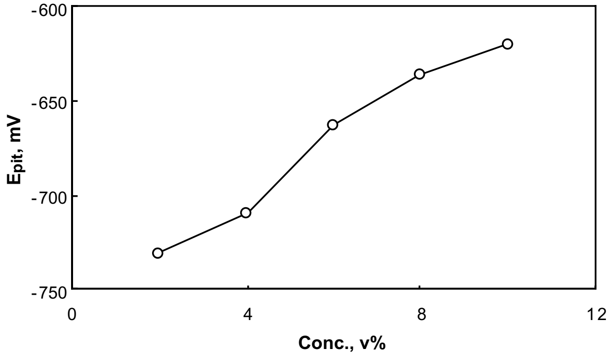

Fig. 6. Relationship between extract concentration and E_{pit}.

The shift in the pitting potential increases as the inhibitor concentration is increased. However, the relation between the pitting potential and inhibitor concentration is not linear as shown in Fig. 6. Thus, in relatively high concentrations the extent of the anodic shift in pitting potential decreases.

4. Conclusion

1. The prickly pear extract acts as a good inhibitor for corrosion of aluminum in 2.0 M HCl solution. The IE increases with increasing extract concentration.
2. The inhibition action is performed via adsorption of the extract compounds on aluminum surface. The adsorption process is spontaneous and follows Langmuir adsorption isotherm.
3. The increase of temperature decreases the IE of the extract. The adsorption process may be physical in nature.
4. The presence of the extract increases the activation energy of the corrosion reaction.
5. The *Opuntia* extract provide some protection against pitting corrosion of aluminum in presence of chloride ions. The degree of protection increases with increasing extract concentration.

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