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# Inhibition of acid corrosion of aluminum using vanillin

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**Abstract**

The inhibition efficiency (IE) of vanillin towards the corrosion of aluminum in 5 M HCl solution was measured using weight loss measurement, hydrogen evolution method, thermometry and potentiostatic polarization techniques. The results drawn from the different techniques are comparable and exhibit a small discrepancy. It was found that vanillin acts as a good inhibitor for the corrosion of aluminum in 5 M HCl solution. The IE increases as the concentration of vanillin is increased. The inhibition action of vanillin is discussed in view of the adsorption of its molecules on the electrode surface through the active centers contained in its structure. It was found also that adsorption of vanillin on aluminum surface follows Langmiur adsorption isotherm. 

## 1. Introduction

Aluminum has a remarkable economic and industrial importance owing to its low cost, lightweight, high thermal and electrical conductivity. The most important feature in aluminum is its corrosion resistance due to the formation of a protective film on its surface upon its exposure to atmosphere or aqueous solutions. Many researches were devoted to study the corrosion of aluminum in the different aqueous solutions [1–3]. Hydrochloric acid solutions are used for pickling of aluminum or for its chemical or electrochemical etching. It is very important to add a corrosion inhibitor to decrease the rate of aluminum dissolution in such solutions. The inhibition of aluminum corrosion in acidic solutions was extensively studied using organic and inorganic compounds [4–11]. It was found that the organic compounds are effective corrosion inhibitors due to their ability to form an adsorbed protective film at the metal surface. The adsorption of carbonyl compounds on the metal surface was shown to occur through their carbonyl group [12]. Vanillin is an aromatic aldehyde


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that possesses a pleasant fragrance. Vanillin is the key component in vanilla flavoring and can be found in perfumes and other scented products, as well. Very little information is known about the use of vanillin as corrosion inhibitor for metals.

The objective of the present work is to study the inhibitive action of vanillin toward the corrosion of aluminum in 5 M hydrochloric acid solution. Weight loss measurements, hydrogen evolution method, thermometry and potentiostatic techniques were used to evaluate the inhibition efficiency (IE) of vanillin.

## 2. Experimental method

Aluminum metal with purity of 99.99% provided by the "Aluminum Company of Egypt, Nagh ammady" was used in the present study. Aluminum sheets with double side's surface area of 1 $cm^2$ were used for weight loss, thermometry and hydrogen evolution measurements. The aluminum sheets were bent into a U form and introduced into the test solutions with their edges downward. A new test piece was used for each experiment. 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.

A stock solution of vanillin, 4-hydroxy-3-methoxy benzaldehyde (melting point, 83°C) was prepared by dissolving it in 20/80 ethyl alcohol–water mixture. To prepare the desired concentration, a specific volume was taken from the stock solution and added directly to the aqueous solution.

Weight loss measurements were carried out as described elsewhere [13]. The IE was calculated using the following equation:

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

where $w$ and $w_{\mathrm{i}}$ are the weight loss of aluminum coupon in free and inhibited acid solutions, respectively.

Potentiostatic polarization studies were carried out using EG&G model 173 potentiostat/galvanostat. Three-compartment cell with a saturated calomel reference electrode and a platinum foil auxiliary electrode was used.

The reaction vessel used in thermometry experiments was basically the same as described by Mylius [14]. The Mylius vessel was kept in thermos to be thermally isolated from the surrounding during the whole experiment time. Exactly, 20 ml of test solution was used for each experiment. The mercury reservoir of the used thermometer was rested on the aluminum specimen. The variation in temperature of the system is measured to $\pm 0.5$°C as a function of time. The term reaction number (RN) was used by Mylius to represent the rate of corrosion drawn from thermometry technique. The RN was defined by Mylius as:

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

where $T_{\mathrm{m}}$ and $T_{\mathrm{i}}$ are the maximum and initial temperatures, respectively and $t$ is the time in minutes elapsed to reach $T_{\mathrm{m}}$. It is clear from this definition that, easily corroding metals are characterized by high RN values through an increase in $T_m$ and/or diminution of $t$. The IE is calculated as the percent reduction in the RN:

$$IE = [(RN_f - RN_i)/RN_f] \times 100$$

where $RN_f$ and $RN_i$ are the reaction numbers of aluminum dissolution in free acid and in presence of vanillin, 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 [15]. All chemicals used for preparing the test solutions were of analytical grade and the experiments were carried out at room temperature, $30 \pm 1°C$.

## 3. Results and discussion

### 3.1. Weight loss measurements

The loss in weight of aluminum strips in 5 M HCl in absence and in presence of different concentrations of vanillin, for 1 h, was determined. The IE was calculated and represented in Table 1. Inspection of the data in Table 1 reveals that vanillin acts as a very good inhibitor for corrosion of aluminum in hydrochloric acid. The IE of vanillin increases with the increase of its concentration.

Vanillin is an aromatic aldehyde containing carbonyl, methoxy and hydroxyl groups arranged around the aromatic ring. The adsorption of vanillin on aluminum surface would take place through all these functional groups. This simultaneous adsorption of the three groups forces the vanillin molecule to be horizontally oriented at the metal surface. The area of the surface covered by one molecule is the maximum in case of horizontal orientation of the adsorbed molecules. This situation results in high protection efficiency even in case of low inhibitor concentrations. As the inhibitor concentration is increased, the part of the metal surface covered by inhibitor molecule increases leading to an increase in IE.

A parameter ($\theta$), which represent the part of the metal surface covered by the inhibitor molecules was calculated for different inhibitor concentrations and represented in Table 1. Inspection of Table 1 reveals that $\theta$ increases as the inhibitor concentration ($C$) is increased. Plotting $C/\theta$ against $C$ gives a straight line with unit slope value (Fig. 1) indicating that adsorption of vanillin on aluminum surface

Table 1
Effect of vanillin concentration on its IE for aluminum corrosion in 5 M HCl solution as obtained from weight loss measurements (immersion period, 1 h)

| Vanillin concentration (ppm) | IE% | $\theta$ |
|---|---|---|
| 200 | 93.49 | 0.9349 |
| 1000 | 96.29 | 0.9629 |
| 2000 | 98.16 | 0.9816 |
| 3000 | 98.74 | 0.9874 |
| 4000 | 98.99 | 0.9899 |

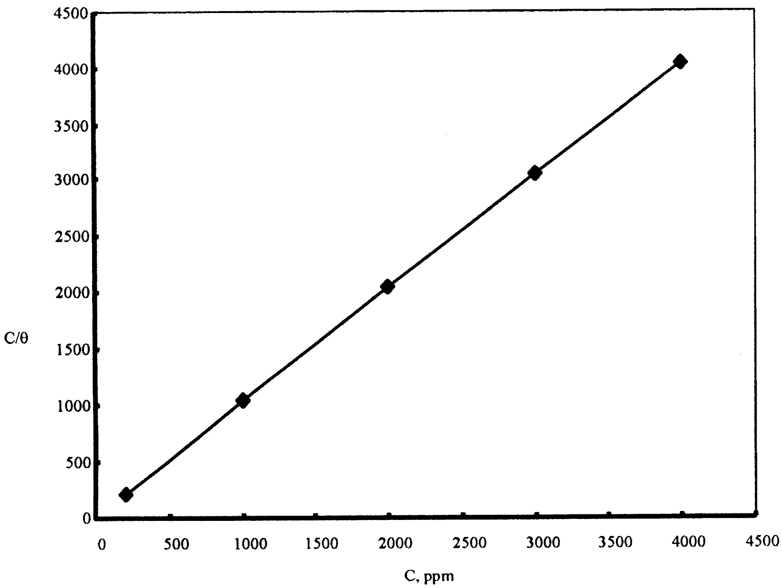


Fig. 1. Relationship between vanillin concentration ($C$) and $C/\theta$.

follows Langmuir adsorption isotherm. From this result it could be concluded that there is no interaction between the molecules adsorbed at the metal surface.

### *3.2. Thermometry*

Temperature change of the system involving aluminum in 5 M HCl was followed as a function of time in absence and in presence of different vanillin concentrations (Fig. 2). The maximum temperature ($T_m$) measured in the free acid solution is 76°C and was attained after time ($t$) of 36 min. This corresponds to a RN of 1.25°C/min. Addition of vanillin caused a decrease in the maximum temperature and an increase in the time required to reach it. This indicates that vanillin retards the dissolution rate of aluminum in the acidic solution, presumably by its adsorption on the metal surface. The extent of inhibition depends on the degree of coverage of the metal by the adsorbed molecules. Strong adsorption is noted for vanillin, since a simultaneous increase in $t$ and decrease in $T_m$ take place, and both the factors cause a large decrease in the RN of the system.

Increasing the vanillin concentration in the acid solution decreases the RN of aluminum dissolution and consequently the IE is increased. Fig. 3 represents the relationship between vanillin concentration and IE. Inspection of Fig. 3 reveals that, there is a rapid increase in the IE with an increase in vanillin concentration until a certain concentration, after which the increase of vanillin concentration causes a small increase in IE. In fact, the curve of Fig. 3 is similar to the adsorption isotherm.

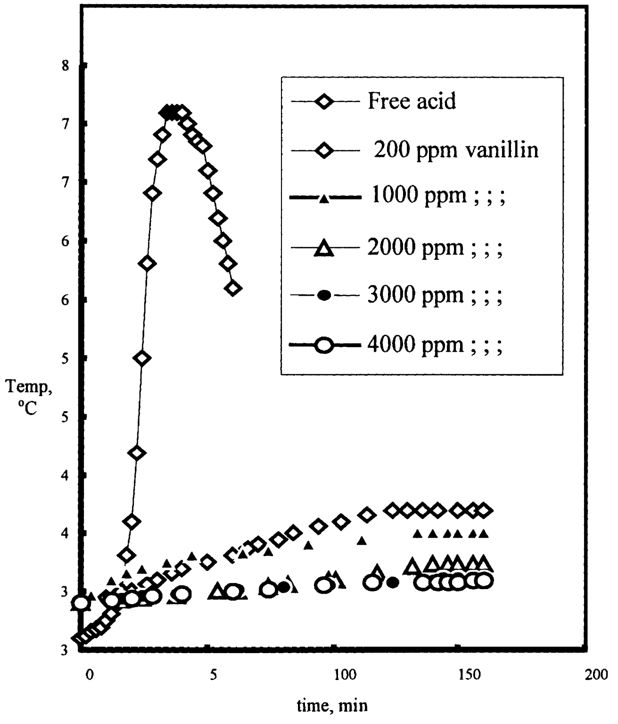


Fig. 2. Thermometric curves of aluminum in free and inhibited acid solutions.

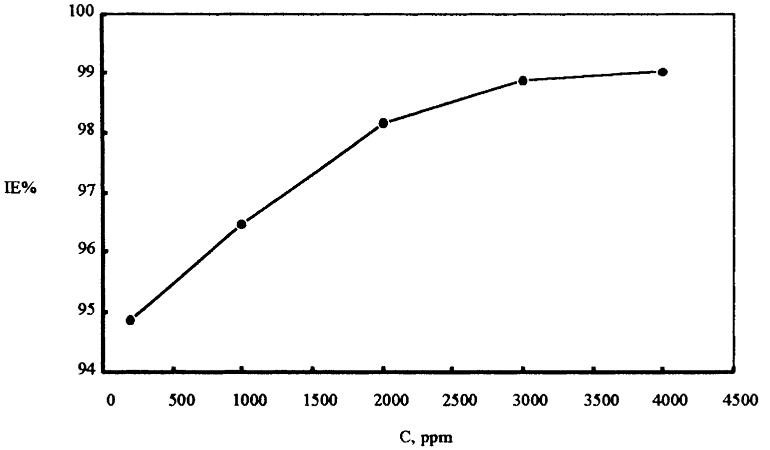


Fig. 3. Relationship between vanillin concentration (*C*) and IE% as obtained from thermometry technique.

The concentration at which the IE starts to change slowly may be taken as indication to the completion of a monolayer.

### 3.3. Hydrogen evolution measurements

The dissolution reaction of aluminum in 5 M HCl devoid of and containing different concentrations of vanillin was studied using hydrogen evolution method. The relationship between the volume of hydrogen evolved during the corrosion reaction and the reaction time is represented in Fig. 4. Inspection of the figure reveals that, there is a linear relation between hydrogen volume and time. The rate of hydrogen evolution is very small at the beginning of the reaction, then after certain time it increases markedly. The initial time interval through which the rate of reaction is very small is the incubation period. During this incubation period, the breakdown of the pre-immersed oxide film on the metal surface takes place before the start of metal attack.

Further inspection of the curves of Fig. 4 reveals that the addition of vanillin reduces markedly the rate of hydrogen evolution. As the vanillin concentration is increased, the rate of hydrogen evolution decreases. Since aluminum is readily soluble in aqueous acidic solutions with the liberation of hydrogen, the rate of hydrogen liberation corresponds to aluminum corrosion rate. So, the slopes of the straight portions of the curves, after the incubation period, were taken as a measure of the corrosion rates of aluminum in free ($R_f$) and inhibited ($R_i$) acid solutions. The IE is calculated as follows:

$$\mathrm{IE} = [(R_f - R_i)/R_f] \times 100$$

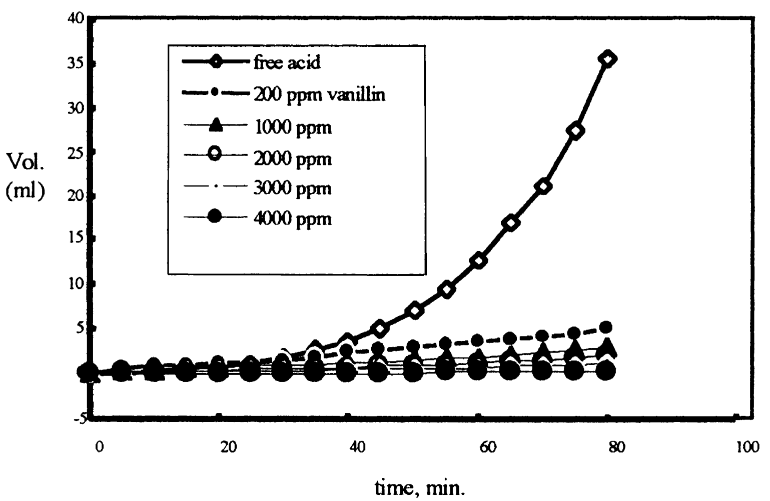


Fig. 4. Hydrogen evolution during corrosion of aluminum in free and inhibited acid solutions.

Table 2
IE of different concentrations of vanillin toward aluminum corrosion in 5 M HCl solution

| Vanillin concentration (ppm) | IE% |
|---|---|
| 200 | 95.8 |
| 1000 | 97.2 |
| 2000 | 97.9 |
| 3000 | 99.3 |
| 4000 | 99.8 |

The values of IEs of different concentrations of vanillin are given in Table 2. These values show that the IEs of the vanillin are very high at all concentrations and comparable with those obtained from weight loss and thermometric techniques.

### 3.4. Potentiostatic polarization

Fig. 5 shows the effect of vanillin concentration on the anodic and cathodic polarization curves of aluminum in 5 M HCl solution. Inspection of Fig. 5 reveals that the presence of increasing concentrations of vanillin cause a markedly decrease in the corrosion rate i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be ascribed to adsorption of vanillin molecules over the corroded surface. The electrochemical parameters, corrosion potential ($E_{corr}$), corrosion rate ($I_{corr}$), anodic Tafel constant ($\beta_a$), cathodic Tafel constant ($\beta_c$) and inhibition efficiency (IE%), were calculated from the curves of Fig. 5 and given in Table 3. Inspection of Table 3 reveals that the corrosion potential is slightly shifted to more noble direction as the vanillin concentration is

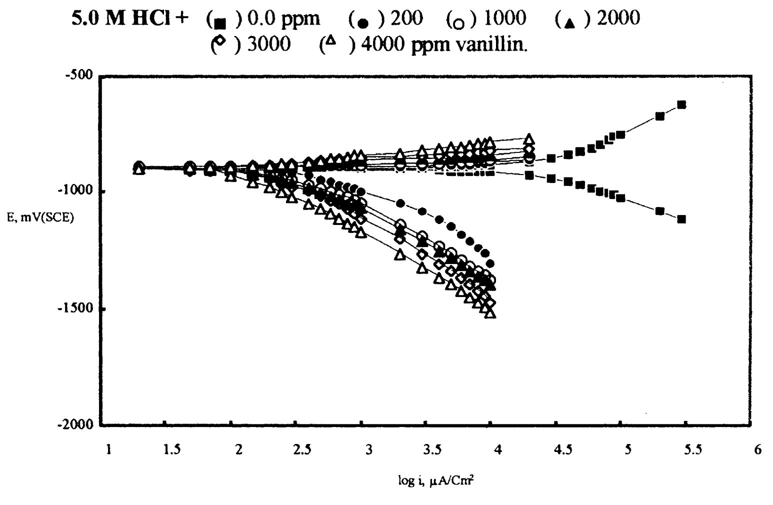


Fig. 5. Potentiostatic polarization curves of aluminum electrode in 5 M HCl avoid of and containing different vanillin concentrations.

Table 3
Electrochemical parameters for aluminum in free and inhibited HCl solutions

| Vanillin concentration (ppm) | $E_{corr}$ (mV(SCE)) | $I_{corr}$ (μA/cm$^2$) | IE% | $\beta_a$ (mV decade$^{-1}$) | $\beta_c$ (mV decade$^{-1}$) |
|---|---|---|---|---|---|
| 0 | −902 | 2591.31 | – | 180 | 188 |
| 200 | −898 | 99.96 | 96.14 | 60 | 342 |
| 1000 | −893 | 35.61 | 98.62 | 58 | 316 |
| 2000 | −890 | 28.06 | 98.91 | 58 | 282 |
| 3000 | −888 | 18.86 | 99.27 | 57 | 299 |
| 4000 | −888 | 13.73 | 99.47 | 59 | 299 |

increased. Moreover, the corrosion current decreases markedly and the IE increases with an increase in vanillin concentration.

Further inspection of Table 3 reveals that both anodic and cathodic Tafel slopes decrease markedly upon addition of increasing concentrations of vanillin. This large change in anodic and cathodic Tafel slopes in presence of vanillin indicates that the latter affects both anodic and cathodic reactions. Therefore, vanillin can be arranged as mixed inhibitor.

Thus, the IEs which were evaluated, for vanillin towards the acid corrosion of aluminum, using the four above techniques show an agreement and conformity of the experimental results. However, there are small differences in the absolute values obtained from the different techniques. This observed discrepancy could be attributed to the different experimental conditions under which each technique was carried out.

## 4. Conclusions

1. Vanillin acts as a very good inhibitor for corrosion of aluminum in high concentrated hydrochloric acid.
2. The high IE of vanillin is attributed to adsorption of its molecules, probably horizontally oriented, on aluminum surface.
3. The adsorption of vanillin on aluminum surface follows Langmuir adsorption isotherm. Thus, there is no interaction between the adsorbed molecules.

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