Research Article

Naturally Occurring *Elettaria cardamomum* Extract as a Corrosion Inhibitor for the Dissolution of Zinc in 1.0 M HCl

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The inhibitive action of water extract of naturally occurring *Elettaria cardamomum* plant against the corrosion of zinc in 1.0 M HCl solution was investigated using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy. From these measurements, it was found that the values of surface coverage (θ) and inhibition efficiency increase with increasing the concentration of the extracted compound. The activation energy of the corrosion was calculated and it was found that the presence of the extracted compound in 1.0 M HCl solutions increases the values of activation energy. The inhibiting effect of this extract results from its adsorption on the electrode surface via the adsorption centers of the compounds present in the extract. The adsorption of this extract compound onto the surface of zinc follows the Langmuir adsorption isotherm. The thermodynamic parameters were calculated for the tested system from the data obtained at different temperatures.

1. Introduction

Corrosion of zinc has been a subject of numerous studies due to its high technological value and wide range of industrial applications and economic importance; its protection against corrosion has attracted much attention. The use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media [1]. Most of the well-known corrosion inhibitors are organic compounds containing nitrogen, sulphur, and oxygen atoms [2–7]. This study sets out to develop a safe method of corrosion protection, harmless to nature but still effective against corrosion, by searching for natural products. The purpose of this study wants to discover new, environmentally friendly corrosion inhibitors, that is, material protection compounds, based on components from naturally occurring. Recently, plant extracts have again become important as an environmentally acceptable, readily available, and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [8].

Elettaria cardamomum Maton is an important member of the family Zingiberaceae. The seeds contain essential oil

in concentration of about 4% of dry weight. The main compound is 1,8-cineole (representing 50% or more), with smaller amounts of α -terpineol and limonene [9, 10].

The present work aims to study the effect of dry fruits extracts of *E. cardamomum* as a corrosion inhibitor for the corrosion of zinc in 1.0 M HCl. Moreover, the effect of temperature on the dissolution of zinc as well as on the inhibition efficiency of the used compound was also investigated.

2. Experimental

2.1. Medium. The aggressive solution of 1.0 M HCl was prepared by dilution of analytical grade HCl (37%) with double distilled water and all experiments were carried out in unstirred solutions.

2.1.1. Extract Preparation. Dry fruits of *E. cardamomum* were extensively washed under running tap water for removal of dust particles and epiphytic hosts normally found on the surface, followed by washing with sterilized distilled water. They were further air-dried on filter paper at room temperature and then powdered with the help of sterilized

SCHEME 1

pestle and mortar. Dry powder was further extracted by using aqueous solvents [11, 12] as follows.

2.1.2. Aqueous Extraction. Air-dried powder (10 g) of the respective plant part was mixed well in 100 mL sterilized distilled water and kept at room temperature for 24 h on an orbital shaker with 150 rpm. The solution was further filtered using muslin cloth. The filtrate was centrifuged at 5000 rpm for 15 min. The supernatant thus obtained was filtered through Whatman's filter no. 1, then the filtrate was collected in a preweighed sterilized test tube. Aqueous extracts were prepared in a final concentration of 100 mg/mL. The extract main components have the formulas shown in Scheme 1.

2.2. Weight Loss Measurements. Zinc strips (99.99% pure), with $3.0 \times 2.0 \times 0.05$ cm sizes for each, were used for weight loss measurements. Weight loss experiments were carried out as described elsewhere [13]. The corrosion rate (CR) and the percentage protection efficiency IE (%) were calculated according to the following equations [14, 15]:

$$\text{CR} = \frac{\Delta m}{St}, \quad (1)$$

$$\text{IE (\%)} = \frac{\text{CR}_{\text{corr}} - \text{CR}_{\text{corr(inh)}}}{\text{CR}_{\text{corr}}} \times 100,$$

where Δm (mg) is the mass loss, S (dm^2) is the area, t (h) is the immersion period, and CR_{corr} and $\text{CR}_{\text{corr(inh)}}$ are the corrosion rates of zinc in the absence and presence of the inhibitors.

2.3. Potentiodynamic Polarization. Potentiodynamic measurements were carried out using three-compartment glass cell and PS remote potentiostat and PS6 software for calculation of electrochemical parameters. Platinum electrode was used as a counter electrode (separated from the cell solution by a sintered glass frit) and a saturated calomel electrode SCE (inside a Luggin probe) as a reference electrode. A cylindrical rod embedded in araldite with an exposed surface area of 0.5 cm^2 was used. The electrode surface was polished with different grades of emery paper, degreased with acetone, and rinsed with distilled water.

The inhibition efficiency IE (%) was calculated from polarization measurements according to the relation given below:

$$\text{IE (\%)} = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100, \quad (2)$$

where I_{corr} and $I_{\text{corr(inh)}}$ are uninhibited and inhibited corrosion current densities, respectively. They are determined by extrapolation of Tafel lines to the respective corrosion potentials.

2.4. Electrochemical Impedance Spectroscopy. The impedance measurements were carried out at open circuit potential (E_{ocp}) in the frequency range from 10 kHz to 100 mHz with signal amplitude perturbation of 5 mV by using a computer-controlled potentiostat (Auto Lab 30, Metrohm). All experiments were performed using three-electrode system.

The surface coverage and the inhibition efficiency of the inhibitor were calculated from the charge transfer resistance values using the following equations:

$$\theta = \frac{(1/R_{\text{ct}})_o - (1/R_{\text{ct}})}{(1/R_{\text{ct}})_o}, \quad (3)$$

$$\text{IE (\%)} = \frac{(1/R_{\text{ct}})_o - (1/R_{\text{ct}})}{(1/R_{\text{ct}})_o} \times 100,$$

where $(R_{\text{ct}})_o$ and (R_{ct}) are the uninhibited and inhibited charge transfer resistance, respectively [16].

3. Result and Discussion

3.1. Weight Loss Measurements. The effect of addition of the extracted compound on the weight loss of zinc strips in 1.0 M HCl as a corrosive medium was studied. The values of percentage inhibition efficiency IE (%) and corrosion rate (CR) obtained from weight loss method at different concentrations of inhibitor at 30°C are summarized in Table 1. It has been found that this compound inhibits the corrosion of zinc in hydrochloric acid solution, at all concentrations used in this study, that is, 100–500 ppm. The data given in Table 1 reveals that the corrosion rate is decreased from 252.9 to $16.20 \text{ mg dm}^{-2} \text{ h}^{-1}$.

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior [17]. The values of surface coverage ($\theta = \text{IE}/100$) for different concentrations of the studied natural extract obtained from the weight loss measurements at temperature range 303 K. Data were tested graphically by fitting to various isotherms. A straight line (Figure 1) was obtained on plotting C_{inh} versus C_{inh}/θ . From this plot, it is observed that it obeys Langmuir's adsorption isotherm

$$\theta = \frac{W_o - W}{W_o}. \quad (4)$$

3.2. Polarization Studies. The effect of addition of various concentrations of the natural extracted compound on the cathodic and anodic polarization curves of zinc in 1.0 M HCl

TABLE 1: Corrosion parameters for zinc in an aqueous solution of 1.0 M HCl in absence and presence of different concentrations of inhibitor from weight loss measurements at 30°C for 1/2 h.

Inhibitor concentration (ppm)	Weight loss (mg dm ⁻²)	CR (mg dm ⁻² h ⁻¹)	IE (%)
Blank	843	252.90	—
100	311	93.30	63.10
200	206	61.80	75.60
300	151	45.30	82.00
400	74	22.20	91.30
500	54	16.20	93.60

FIGURE 1: Langmuir's adsorption isotherm plot for the adsorption of inhibitor in 1.0 M HCl, on the surface of zinc.

solution at 30°C (Figure 2) was studied. Electrochemical parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel constants (b_a and b_c), and percentage inhibition efficiency IE (%) were calculated from Tafel plots shown in Table 2. It is evident from the table that there is an increase in both anodic and cathodic Tafel slopes upon addition of the inhibitor indicated a mixed anodic and cathodic effect on the corrosion inhibition mechanism [18]. It is also observed from the table that the corrosion potential shifted to more positive values and i_{corr} decreased when the concentration of the inhibitor was increased indicating the inhibiting effect of this compound resulting in an increase on IE (%) with the increase in the concentration of the additive.

3.3. Effect of Temperature. The effect of temperature is an important parameter in studies on metal dissolution. The corrosion rate in acid solutions, for example, increases exponentially with a temperature increase because the hydrogen evolution overpotential decreases [19].

The effect of temperature on the corrosion parameters such as i_{corr} , E_{corr} , and IE (%) was studied in 1.0 M HCl alone and in the presence of 500 ppm of inhibitor over the temperature ranges from 303 to 353 K.

The data listed in Table 3 show that E_{corr} shifted to more negative values, whereas the values of i_{corr} increased with the increase in temperature, but by different amounts, indicating that the natural extracted compound affected the

FIGURE 2: Potentiodynamic polarization curves of zinc electrode in 1.0 M HCl solution containing different concentrations of inhibitor at 30°C. (1) 0.00 ppm, (2) 100 ppm, (3) 200 ppm, (4) 300 ppm, (5) 400 ppm, and (6) 500 ppm.

zinc electrochemical dissolution. On the other hand, the increase in temperature led to a decrease in the inhibition efficiency and the best inhibition efficiency was obtained at 303 K.

Arrhenius-type dependence is observed between the corrosion rate and temperature which given by [20]

$$K = \frac{Ae^{-E_a}}{RT}, \quad (5)$$

where K is the rate constant of the metal dissolution reaction that is directly related to corrosion current density i_{corr} [21], A is the frequency factor, T is the absolute temperature, and E_a is the activation energy. By plotting $\log K$ versus $1/T$ the values of E_a can be calculated from the slope of the obtained straight lines (Figure 3). The E_a determined from the Arrhenius plots corresponds to 9.832 kJ mol⁻¹ in the absence and 14.768 kJ mol⁻¹ in the presence of inhibitor. From the obtained values, it is clear that the presence of the natural extracted compound increased the activation energy values and consequently decreased the corrosion rate of the metal. These findings indicate that extracted compound acted as an inhibitor through increasing the activation energy of metal dissolution by making a barrier to mass and charge transfer by their adsorption on metal surface.

TABLE 2: Electrochemical parameters for zinc in absence and presence of different concentrations of inhibitor in 1.0 M HCl solution at 30°C obtained from Tafel polarization curves.

Inhibitor concentration (ppm)	$-E_{\text{corr}}$ (mV SCE)	b_a (mV dec $^{-1}$)	b_c (mV dec $^{-1}$)	I_{corr} (mA cm $^{-2}$)	θ	IE (%)
HCl (1 M)	996	0.43	0.49	2.41	—	—
100	992	0.58	0.59	0.91	0.62	62.30
200	985	0.66	0.64	0.62	0.74	74.30
300	981	0.76	0.72	0.43	0.82	82.20
400	980	0.86	0.76	0.22	0.90	90.90
500	977	0.88	0.81	0.15	0.93	93.80

TABLE 3: Effect of temperature on the corrosion parameters of zinc in 1.0 M HCl and 1.0 M HCl + 500 ppm of inhibitor.

System	T (K)	E_{corr} (mV SCE)	I_{corr} (Ma cm $^{-2}$)	IE (%)
1.0 M HCl	303	−996	2.41	—
	313	−1002	2.81	—
	323	−1001	3.96	—
	333	−999	4.73	—
	343	−1001	5.58	—
1.0 M HCl + 500 ppm inhibitor	303	−977	0.15	93.80
	313	−979	0.231	91.70
	323	−983	0.322	91.80
	333	−985	0.445	90.50
	343	−987	0.561	89.90

FIGURE 3: Relation between $\log K$ and the reciprocal of the absolute temperature of zinc electrode in 1.0 M HCl devoid of and containing 500 ppm of an inhibitor compound.

FIGURE 4: Arrhenius' plot of $\log K/T$ versus $1/T$ for the dissolution of zinc in 1.0 M HCl in the absence and presence of inhibitor.

An alternative formulation of the Arrhenius equation is the transition state equation [22, 23]

$$K = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right), \quad (6)$$

where h is Planck's constant, N is Avogadro's number, ΔS^* is the entropy of activation, and ΔH^* is the enthalpy of activation.

Figure 4 shows a plot of $\log(K/T)$ against $(1/T)$. Straight lines are obtained with a slope of $(-\Delta H^*/2.303R)$ and an intercept of $(\log R/Nh + S^*/2.303R)$ from which the values of ΔH^* and ΔS^* are calculated and listed in Table 4.

As it can be seen from Table 4, the positive values of ΔH^* reflect a strong chemisorption of the inhibitor on the surface. The values of entropy of activation ΔS^* in the absence and presence of the studied extract compound are negative. This implies that the activated complex in the rate

TABLE 4: Activation parameters of the dissolution reaction of zinc in 1.0 M HCl in the absence and presence of 500 ppm of inhibitor.

System	E_a (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹)
1.0 M HCl	9.832	16.12	-209.355
1.0 M HCl + 500 ppm inhibitor	14.768	25.12	-216.105

TABLE 5: Impedance data and surface coverage for zinc electrode in 1.0 M HCl in absence and presence of different concentrations of inhibitor.

Inhibitor conc. (ppm)	R_s (Ω cm ²)	R_{ct} (Ω cm ²)	C_{dl} (μ F cm ⁻²)	θ	IE (%)
0.00	0.95	51	22.30	—	—
100	1.20	230	19.80	0.78	77.80
200	1.42	345	17.33	0.85	85.20
300	2.02	378	15.47	0.86	86.50
400	2.30	418	11.08	0.87	87.80
500	2.85	470	9.78	0.89	89.20

FIGURE 5: Electrical equivalent circuit (R_s Ω : uncompensated solution resistance, R_{ct} : charge transfer resistance, and C_{dl} : double layer capacitance).

determining step represents an association rather than a dissociation step [23].

3.4. Electrochemical Impedance Spectroscopy Studies. Electrochemical impedance spectroscopy (EIS) measurements were carried over the frequency range from 10 kHz to 100 mHz at open circuit potential. The sample equivalent Randle circuit for studies is shown in Figure 5 obtained for zinc in 1.0 M HCl with and without inhibitor, where R_s (Ω cm²) represents the solution and corrosion products film; the parallel combination of resistor, R_{ct} (charge transfer resistance), and capacitor C_{dl} (double layer capacitance) which represents the corroding interface.

Figure 6 shows the Nyquist plots for zinc in 1.0 M HCl solution without and with different concentrations of inhibitor at 30°C. The Nyquist plots were regarded as one part of a semicircle. The charge transfer resistance values (R_{ct}) were calculated from the difference in impedance at lower and higher frequencies, as suggested by Haruyama and Tsuru [24].

The impedance quantitative results were listed in Table 5. It is seen that the R_{ct} values of the investigated compounds increase with increasing inhibitor concentration. At the same time the C_{dl} has opposite trend in the whole concentration range. These observations clearly bring out the fact that the corrosion of zinc in 1.0 M HCl is controlled by a charge transfer process. The decrease of C_{dl} by the increase of

FIGURE 6: The Nyquist plots for zinc electrode in 1.0 M HCl in absence and presence of different concentrations of inhibitor: (1) 0.00 ppm, (2) 100 ppm, (3) 200 ppm, (4) 300 ppm, (5) 400 ppm, and (6) 500 ppm.

the inhibitor concentration is due to the adsorption of the inhibitor compound on the electrode surface leading to a film formation on the Zn surface, and then decreasing the extent of dissolution reaction [25].

4. Inhibition Mechanism

The inhibitive effect of the investigated water extract as mentioned above from the experimental results was a retardation of the dissolution process of zinc metal in HCl solution. It can be proposed that the effective compounds in this extract contain functional groups, which can operate as adsorption centers.

The shape of the molecule and its size and the presence of conjugate double bonds and other groups (such as OH) in α -terpineol and the oxygen in 1,8-cineole, which are electron rich and serve as good adsorption sites onto the metal surface, are therefore responsible for the inhibitory action of the investigated extract on zinc in HCl solutions.

The adsorption of an organic adsorbate on the surface of a metal can be regarded as a substitutional adsorption process between organic compound in aqueous phase and water molecules adsorbed onto the electrode surface [26]

where (x) is the size ratio, which is the number of water molecules replaced by one molecule of organic adsorbate. The above process attains equilibrium when

where μ is the chemical potential.

5. Conclusions

- (1) There is a good agreement among the results obtained by different techniques of measurements.
- (2) *E. cardamomum* extract have high inhibitory effect on the corrosion of zinc in 1.0 M HCl and the inhibition efficiency increase with increasing its concentration.
- (3) The inhibitory effect of *E. cardamomum* extract results from its adsorption on the metallic surface through its electron rich functional groups.
- (4) The adsorption of the investigated water extract on a zinc surface follows Langmuir's adsorption isotherm.

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