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Inhibition of C-steel corrosion in acidic solution using the aqueous extract of zallouh root

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Abstract

The inhibitive action of the aqueous extract of the root of shirsh el zallouh (*Ferula harmonis*) toward the corrosion of C-steel in HCl solution was investigated. The inhibition efficiency was measured using weight loss and potentiostatic polarization techniques. The electrochemical behavior of the extract was investigated using cyclic voltammetry. It was found that the addition of the extract reduces the corrosion rate of C-steel. The inhibition efficiency increases with increasing extract concentration. The inhibitive effect of the tested extract was discussed in view of adsorption of its components on the steel surface. The adsorption of the extract components on the C-steel surface follows Langmuir adsorption isotherm. The inhibition efficiency decreases as the temperature is increased. The presence of extract increases the activation energy of the corrosion process of C-steel. The curves of cyclic voltammetry technique showed that the adsorbed molecules reduce the charge density on the steel surface.
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1. Introduction

C-steel is one of the most important alloys which frequently used in wide industrial applications. In particularly, it used in manufacture of petroleum pipe lines, pumping stations for agricultural water irrigation. Corrosion problems arise as a result of interaction of the aqueous solutions with C-steel, especially during the pickling process in which the alloy is brought in contact with high concentrated acids. This process can lead to high economic loss due to the corrosion of the alloy. Thus, the pickling acid solutions must contain some compounds to prevent the corrosion of the steel. Many researches were devoted to investigate hundreds of organic and inorganic compounds as inhibitors for C-steel corrosion in different aggressive solutions [1–6]. Although many of these tested compounds have high inhibition efficiencies, the usage of them still undesired due to their dangerous effects on human and environment as well as their high prices.

In the recent years, there is an increasing awareness of environment and green chemistry. Therefore, many works were conducted to use the environment friendly substances, as corrosion inhibitors, instead of the harmful synthetic chemicals

[7–11]. It should be mentioned here that the first used corrosion inhibitors were naturally occurring substances extracted from various parts of different plants. Beside there safely handling, plant extracts are usually cheap and could be obtained by simple extraction process.

The present work is devoted to test the aqueous extract of the hairy root of shirsh el zallouh (*Ferula harmonis*) as corrosion inhibitor for C-steel in HCl solution. Shirsh el zallouh is a small herb, a relative of the carrot family (Umbelliferae), with thin leaves and tiny white or yellow flowers. The plant grows between 6000 and 10,000 feet elevation around massive Mount Haramoun, in the Middle East. The extract of its root was used in folk remedy as it contains many compounds which dilate blood vessels and stimulate circulation. Weight loss measurements and polarization technique were used for evaluation of the inhibition efficiencies of the used extract. Cyclic voltammetry technique, were also used for investigation of the electrochemical behavior of the extract.

2. Experimental

ASTM A573 Grade 70 carbon steel, with the chemical composition in Table 1, was used in the present study. The steel specimens were taken from the tanks of Cairo Co. for petroleum refining.

For potentiostatic studies, a cylindrical rod of the steel was embedded in araldite with exposed surface area of 0.38 cm², and used as working electrode.

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Table 1
Chemical composition of the used C-steel

Composition	wt%
C	0.27
Mn	0.85
P	0.035
S	0.035
Si	0.15
Fe	Remainder

Fig. 1. Structure of ferutinol benzoate.

The electrode was polished with different grades of emery papers, degreased with acetone and rinsed by running distilled water, before immersed in the test solution.

Potentiostatic polarization and cyclic voltammetry experiments were carried out using Meinsberger Potentiostat/Galvanostat, with software zum ps6 remote for the calculation of corrosion parameters and charge density. Three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. The potentiostatic curves were obtained by application of potential at a scanning rate of $5\,mV\,s^{-1}$, whereas those of cyclic voltammetry were carried out at $10\,mV\,s^{-1}$. The corrosion current and potential were obtained from the point of intercept of anodic and cathodic Tafel lines using the software. The inhibition efficiency IE was calculated using the following equation:

$$IE = \left[\frac{I - I_i}{I}\right] \times 100$$

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

Coupons of steel with exposed surface area of $4\,cm^2$ (1 cm, 1 cm, 0.5 cm) were used for weight loss measurements. The steel coupons were left hanged in the test solution for 1 day at $25 \pm 1\,^{\circ}C$ before recording the loss of their weights. The corrosion rate was calculated, in milligram per square centimeter per hour $(mg\,cm^{-2}\,h^{-1})$, on the basis of the apparent surface area. The inhibition efficiencies calculations were based on the weight loss measurements at the end of the whole exposure period. The results of the weight loss experiments are the mean of three runs, each with a fresh steel sheet and fresh acid solution. Inhibition efficiency (IE) was calculated from the weight loss measurements using the equation:

$$IE = \left[\frac{W - W_i}{W}\right] \times 100$$

where W and W_i are the weight loss of the coupon in free and inhibited solutions, respectively.

All the chemicals used for preparation of the test solutions were of analytical grade and the experiments were carried out at room temperature, $25 \pm 1\,^{\circ}C$.

The hairy roots of shirsh el zallouh were finely divided and extracted in boiled water for 3 h. The filtrate was then evaporated on steam bath and the sticky solid residue was left overnight in open air for a complete dryness. A stock solution was prepared, by weight, from the collected solid and used then for preparation of the desired concentrations by dilution.
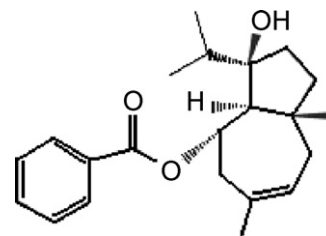
3. Results and discussion

3.1. Weight loss measurements

Table 2 presents the results of weight loss measurements for the corrosion of C-steel, in 2.0 M HCl solutions devoid of and containing different concentrations of the zallouh extract. Inspection of the data in the table reveals that the addition of zallouh extract decreases markedly the corrosion rate of C-steel. This result indicates the inhibitive effect of the added extract on C-steel corrosion in the acidic solution. The inhibition efficiency increases as the concentration of added extract is increased.

It is common practice to assume that the inhibitive effect of the added compound is a result of adsorption of its molecules on the metal surface. Therefore, there is a direct relationship between the inhibition efficiency and the fraction of surface covered by the adsorbed molecules (θ). Thus, the values of (θ) were calculated using the equation ($\theta = IE/100$), for different concentrations of zallouh extract and given in Table 2.

The observed inhibition action of the zallouh extract could be attributed to the adsorption of its components on C-steel surface. The formed layer, of the adsorbed molecules, isolates the metal surface from the aggressive medium leading to decreasing the corrosion rate. The chemical components of the extract of ferula hermonis roots was identified and determined by several separation and analytical techniques [12–16]. It was found that the extract contains mainly derivatives of the sesquiterpene alcohol, jaeschkeanadiol (ferutinol). The principal derivatives present were found to be about 52% benzoate (Fig. 1) and 30% p-hydroxybenzoate (ferutinine). Some other aryl esters of jaeschkeanadiol and epoxyjaeschkeanadiol, as well as α-bisabolol, were present in small amounts.

To find out the mode of adsorption of extract components on C-steel surface, the relationship between extract concentration (C) and the fraction of surface coverage (θ) should be obtained.

Table 2
Weight loss of C-steel in free and inhibited 2 M HCl solutions

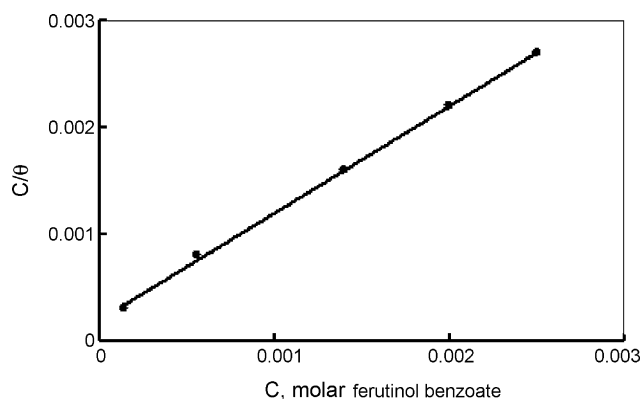| Extract concentration (ppm)	Concentration as molar ferutinol benzoate	Weight loss $(mg\,cm^{-2}\,h^{-1})$	IE%	θ
–	–	0.56	–	–
50	0.00019	0.30	46	0.46
200	0.00076	0.18	68	0.68
500	0.0019	0.13	83	0.83
700	0.0027	0.07	87	0.87
900	0.0034	0.05	91	0.91

Fig. 2. Adsorption isotherm of zallouh components as ferutinol benzoate on C-steel surface in HCl solution.

As has mentioned above, ferutinol benzoate represents the major component of zallouh root extract. Therefore, to evaluate the adsorption parameters, the concentration of zallouh extract is represented, here, as ferutinol benzoate. This is not mean that the ferutinol benzoate is the only compound that responsible for the inhibition action since there are many other components present in the extract. The presence of such compounds, even in small concentrations affects, positively or negatively, the inhibition action of ferutinol benzoate. A graphic representation of the relationship between the extract concentration, calculated as molar ferutinol benzoate (C), and (C/θ) is given in Fig. 2. Inspection of Fig. 2 reveals that, a straight line was obtained with almost unit slope. This result suggests that the adsorption of zallouh components on C-steel surface follows Langmuir adsorption isotherm. Therefore, these findings indicate that, there is no interaction force between the zallouh components adsorbed on C-steel surface.

Langmuir adsorption isotherm could be represented using the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

where K is the adsorption constant and

$$\ln K = \ln \frac{1}{55.5} - \frac{\Delta G_{ad}^{\circ}}{RT}$$

where ΔG_{ad}° is the standard free energy of adsorption where one molecule of water is replaced by one molecule of inhibitor [17] and the numerical value (1/55.5) in the equation stands for the molarity of water. The calculated value of the free energy of adsorption was found to be $-31.0\,kJ\,mol^{-1}$. The negative sign
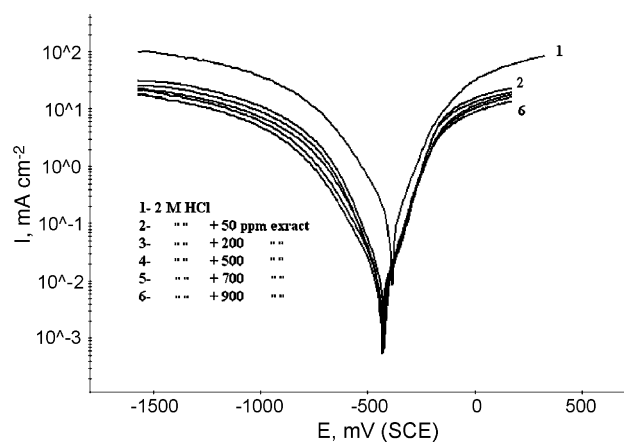

Fig. 3. Anodic and cathodic polarization curves of C-steel in free and inhibited HCl solutions.

indicates that the adsorption of zallouh components on the steel surface is a spontaneous process.

3.2. Potentiostatic polarization

Fig. 3 represents the anodic and cathodic potentiostatic polarization curves of C-steel electrode in solutions of 2.0 M HCl devoid of and containing different concentrations of zallouh extract.

Inspection of Fig. 3 reveals that the polarization curves are shifted toward more negative potentials and less current densities as the concentration of the extract is increased. This behavior indicates the inhibitive action of the added extract on C-steel corrosion in the acid solution.

The corrosion parameters of C-steel electrode in free and inhibited solutions of 2.0 M HCl are given in Table 3. The data of Table 3 reveals that the corrosion potential shifts toward the more negative values as the concentration of the additive is increased. Moreover, the corrosion current density decreases with increasing of additive concentration. It is of interest to note that the values of inhibition efficiencies calculated using polarization technique are comparable with those obtained by weight loss measurements.

Further inspection of Table 3 reveals that, upon addition of extract, the values of both anodic and cathodic Tafel constants decrease markedly. The magnitude of decrement increases as the additive concentration is increased. Moreover, the presence of extract affects the values of both constants almost at the same degree. The variation of the Tafel constants values due to the

Table 3
Corrosion parameters of C-steel corrosion in free and inhibited HCl solutions

Extract concentration (ppm)	E_{corr} (mV)	I_{corr} (mA cm^{-2})	β_a (mV decade^{-1})	$-\beta_c$ (mV decade^{-1})	IE%
0.0	−468	0.42	110	204	–
50	−482	0.21	86	150	50
200	−485	0.17	78	136	59
500	−486	0.10	72	122	76
700	−488	0.05	66	120	88
900	−492	0.03	63	118	93

Fig. 4. Cyclic voltammograms of C-steel in free and inhibited HCl solutions.

Fig. 5. Arrhenius plot for steel corrosion in free and inhibited acid.

presence of zallouh extract indicates that the extract acts as mixed inhibitor.

3.3. Cyclic voltammetry

The cyclic voltammograms of C-steel in solutions of 2 M HCl devoid of and containing two concentrations of zallouh root extract were traced and represented in Fig. 4. The potential was started at −1500 mV and swept in the positive direction up to the oxygen evolution at scanning rate of 10 mV s^{-1}. Inspection of Fig. 4 reveals that the anodic branches of the steel in free and inhibited acid solutions exhibit a narrow passive region with no anodic dissolution peaks. The transpassive region and the onset of oxygen evolution start in both free and inhibited solutions at almost the same potential; about −350 mV.

Further inspection of the curves of Fig. 4 reveals that upon the onset of the transpassive region the current still rising up until the potential is reversed, in case of steel in free acid solution. On the other hand, the current of the transpassive region decreases in the presence of the extract, forming a broad anodic peak. The formation of such peak could be attributed to the adsorption of the extract components on the steel surface. The values of charge density of the transpassive regions were calculated for the three tested solutions and found to be 109, 74 and 65 C for free, 50 and 500 ppm of extract, respectively. It is obvious that the charge density decreases with increasing extract concentration. This result could be interpreted in view of the adsorption of extract components on the steel surface. The adsorbed molecules form a barrier for charge and mass transfer.

3.4. Effect of temperature

The effect of temperature on the corrosion of C-steel in free and inhibited 2 M HCl solutions was studied using potentiostatic polarization in the range of 25–70 °C. The acid solutions were inhibited by addition of 500 ppm of zallouh root extract. It was found that the corrosion rates of steel in both free and inhibited acid media increase as the temperature was increased. However, the extent of the rate increment in the inhibited solution is higher than that in the free acid solution. Therefore, the inhi-
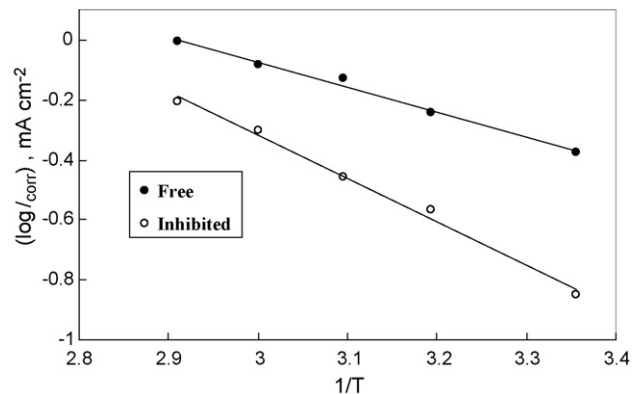
bition efficiency of the zallouh root extract decreases markedly with increasing temperature. This result supports the idea that the adsorption of extract components on the steel surface may be physical in nature. Thus, as the temperature increases the number of adsorbed molecules decreases leading to a decrease in the inhibition efficiency.

The activation energies of corrosion process in free and inhibited acid were calculated using Arrhenius equation:

$$K = A \exp\left(-\frac{E_a}{RT}\right)$$

where E_a is the activation energy, A the frequency factor, T the absolute temperature, R the gas constant and K is the rate constant, which is directly proportion to the corrosion current (I_{corr}). Plotting (log/$_{corr}$) versus $1/T$ gives a straight lines as revealed from Fig. 5. The values of activation energy calculated using the lines of Fig. 5 are 16.08 and 27.69 kJ for free and inhibited acid solutions, respectively. The obtained results suggest that zallouh extract inhibits the corrosion reaction by increasing its activation energy. This could be done by adsorption on the steel surface making a barrier for mass and charge transfer. However, such types of inhibitors perform a good inhibition at ordinary temperature with considerable loss in inhibition efficiency at elevated temperatures [18]. Moreover, the relatively low value of activation energy in presence of zallouh extract suggests a physical adsorption process.

4. Conclusions

- The aqueous extract of zallouh root inhibits the C-steel corrosion in HCl solution.
- The inhibition efficiency increases with increased extract concentration and decreases with increased temperature.
- The inhibitive action of extract was attributed to the adsorption of its components on steel surface.
- The adsorption of extract components follows Langmuir adsorption isotherm.
- The adsorbed molecules decreases the charge density in the transpassive region.

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