Inhibitive effect by extract of *Mentha rotundifolia* leaves on the corrosion of steel in 1 M HCl solution

A. Khadraoui · A. Khelifa · H. Hamitouche ·
R. Mehdaoui

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Abstract An extract of *Mentha rotundifolia* leaves (*EMRL*) was tested as a corrosion inhibitor of steel in 1 M HCl using electrochemical impedance spectroscopy, Tafel polarization methods, and weight loss measurements. The inhibition efficiency of the extract of *Mentha rotundifolia* leaves was calculated and compared. We note good agreement between these methods. The results obtained revealed that the inhibitor tested differently reduced the kinetics of the corrosion process of steel. Its efficiency increases with the concentration and attained 92.87 % at 35 %. The effect of temperature on the corrosion behavior of steel in 1 M HCl was also studied in the range 298 and 338 K. The thermodynamic data of activation were determined. *Mentha rotundifolia* extract is adsorbed on the steel surface according to a Langmuir adsorption model.

Keywords Corrosion · Steel · Green inhibitors · *Mentha rotundifolia* extract · Acid medium

Introduction

Use of inhibitors is one of the most practical methods for protection against corrosion, especially in acid solutions to prevent unexpected metal dissolution and acid consumption [1, 2]. The corrosion inhibitors are one of the largest products within the water treatment chemicals market, and the global corrosion inhibitor market is expected to grow from ca. US\$ 5 billion in 2010 to ca. US\$6 billion in 2015 [3].

A. Khadraoui (✉) · A. Khelifa · H. Hamitouche · R. Mehdaoui
Laboratoire de Génie Chimique, Département de Chimie Industrielle, Faculté de la Technologie,
Université Saâd Dahlab de Blida, BP 270, Route de Soumaâ, 09000 Blida, Algeria
e-mail: khadraoui.abdelkader@gmail.com

The majority of well-known inhibitors are organic compounds containing heteroatoms, such as O, N, S and multiple bonds [4–9]. Most of these organic compounds are not only expensive but also toxic to both human beings and the environment [10], and therefore their use as corrosion inhibitors is limited. Thus, efforts have been made to develop cost-effective and non-toxic corrosion inhibitors. The plant extracts are considered as an incredibly rich source of environmentally acceptable corrosion inhibitors.

This area of research is of much importance because, in addition to being environmentally friendly and ecologically acceptable, plant products are an inexpensive, readily available, and renewable source of materials [11–13].

The use of green corrosion inhibitors such as extracted compounds from leaves or seeds have been widely reported by several authors, including fenugreek, henna, olive, jojoba, black pepper, *Occimum viridis*, *Andrographis paniculata*, *Phyllanthus amarus*, onion, garlic, *Eugenia jambolans*, *Pongamia glabra*, *Opuntia*, eugenol, *Zenthoxylum alatum*, *Nypa fruticans*, *Oxandra asbeckii*, *Ferula assa-foetida*, *Dorema ammoniacum*, *Lavandula angustifolia*, *Justicia gendarussa*, *Gissipium hirsutum*, *Lupinus albus*, *Mentha pulegium*, *Aloe vera*, etc. [14–37].

This paper aimed to study the effect of the extract of *Mentha rotundifolia* leaves (EMRL) on the corrosion of steel in 1 M HCl solution by gravimetric, electrochemical polarization, and EIS methods, the effect of temperature is also studied.

Mentha rotundifolia, which has the current Algerian name is “Timarssat”, belongs to Lamiacea family and is generally found in humid regions of Algeria. The plant grows to about 50–70 cm high. It is an aromatic plant, widely used in traditional medicine. The leaves are very broad, somewhat resembling those of sage, *Salvia* sp., dull green in color and much wrinkled above, often densely woolly and whitish beneath. The flowers are pink or white, in tapering, terminal spikes.

Materials and methods

Plant collection and leaves extract

Mentha rotundifolia was collected in Ain-Defla, Algeria (280 m of altitude), in June 2008. The aerial parts (leaves) of the plant were air-dried in the laboratory at room temperature during several days. Stock solutions of the plant extract were prepared by extracting weighed amounts (10 g) of the powder of the dried leaves for 3 days in 1 M HCl at 298 K with continuous agitation. The solution was filtered and stored. The filtrates from both acid extractions had a reddish-brown appearance. From the stock solutions, inhibitor test solutions were prepared in the concentration range 1–35 % (v/v).

Solutions preparation

The solution 1 M HCl was prepared by dilution of analytical grade 37 % HCl with double-distilled water. The solution tests are freshly prepared before each experiment.

Weight loss measurements

Coupons were cut into $2 \times 1.5 \times 0.2 \text{ cm}^3$ dimensions having composition: 0.13 % C, 0.32 % Si, 0.64 % Mn, 0.15 % Cu, 0.012 % S, 0.01 % P, 0.038 % Al, 0.081 % Cr, 0.011 % Mo, 0.083 % Ni, 0.01 % V and Fe balance, and were used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 280, 400, 600, 800, and 1,200 grades of emery papers. The specimens were washed thoroughly with bidistilled water, degreased with ethanol, and dried before being weighed and immersed in 60 ml of the corrosive medium. The immersion time for the weight loss measurements was 6 h at 298 K.

Electrochemical tests

The electrochemical study was carried out using a EG&G potentiostat/Galvanostat (PAR 273A) piloted by CORR III software. This potentiostat is connected to a cell with three electrode thermostats with a double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was the same used for gravimetric measurements. The surface area exposed to the electrolyte was 0.64 cm^2 . Potentiodynamic polarization curves were plotted at a polarization scan rate of 1 mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarization curves were obtained from -750 to -250 mV at 298 K. The solution test was then de-aerated by bubbling nitrogen. Gas bubbling was maintained prior and through the experiments. The data in the Tafel region have been processed for evaluation corrosion kinetics parameters by plotting the polarization curves. The linear Tafel segments, in a large domain of the potential of the cathodic curves were extrapolated to the corresponding corrosion potentials to obtain the corrosion current values.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with the analyzer of function of transfer model 5210, piloted by Powersuite software. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz, were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments were repeated three times to ensure the reproducibility.

Results and discussion

Weight loss, corrosion rates and inhibition efficiency

The effect of the addition of *EMRL* tested at different concentrations on the corrosion of steel in 1 M HCl solution was studied using weight loss at 298 K after 6 h of immersion period. Inhibition efficiency E (%) is calculated as follows:

Table 1 Gravimetric results of the steel corrosion with and without addition of *EMRL* after 6 h of immersion in 1 M HCl at 298 K

Concentration (%)	W (mg/cm ² h)	E (%)	θ
0	0.1693	–	–
1	0.0980	42.1	0.421
3	0.0835	50.7	0.506
5	0.0753	55.5	0.555
10	0.065	61.6	0.616
15	0.0447	73.6	0.735
20	0.031	81.7	0.816
25	0.0298	82.4	0.823
30	0.027	84.0	0.84
35	0.0265	84.3	0.843

$$E (\%) = \frac{W_{\text{corr}} - W'_{\text{corr}}}{W_{\text{corr}}} \times 100 \quad (1)$$

where W_{corr} and W'_{corr} are the corrosion rate of steel in 1 M HCl in the absence and presence of inhibitor, respectively.

Table 1 gives the values of the corrosion rate (mg cm⁻² h⁻¹), inhibition efficiency (E %), and surface coverage (θ) obtained by E %/100 for steel corrosion in 1 M HCl and in the presence of inhibitors tested at different concentrations.

From Table 1, it can be seen that corrosion rate values in 1 M HCl solution containing *Mentha rotundifolia* extract decreased as the concentration of inhibitor increased. This result is due to the adsorption of components of the extract as coverage of inhibitor on the steel surface increases with inhibitor concentration. The highest inhibition efficiency of 84.34 % was obtained at 35 % of *EMRL*.

This result suggests that an increase in extract concentration increases the number of inhibitor molecules adsorbed onto the steel surface and reduces the surface area that is available for the direct acid attack on the metal surface. The inhibitive effect of the extract of the leaves is ascribed to the presence of organic compounds in the *Mentha rotundifolia* extract which is rich in several organic compounds [38] of high molecular weight with heteroatom and π centers in their molecular structures. The inhibition effect of *EMRL* may be due to the presence of these organic compounds in the extract.

Polarization curves

Potentiodynamic polarization curves of steel in molar HCl in the absence and presence of *EMRL* at different concentrations at 298 K are presented in Fig. 1. The corrosion parameters including corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c), and inhibition efficiency (E %) are collected in Table 2.

Fig. 1 Potentiodynamic polarisation curves of steel in 1 M HCl in the presence of different concentrations of EMRL

Table 2 Electrochemical parameters of steel at various concentrations of EMRL in 1 M HCl and corresponding inhibition efficiency

Concentration (%)	E_{corr} (mV/SCE)	b_c (mV/dec)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E (%)
Blanc	-499	115.4	426.2	–
1	-504.4	119.3	250.1	40.8
3	-506.8	129.7	170.4	59.6
5	-490	118	146.3	65.3
10	-506.8	109.4	112.4	73.4
20	-506.2	117	66.8	84.2
35	-503.2	107	30.1	92.9

In this case, the inhibition efficiency is defined as follows:

$$E (\%) = \left(1 - \frac{I'_{\text{corr}}}{I_{\text{corr}}} \right) \times 100 \quad (2)$$

where I_{corr} and I'_{corr} are current density in the absence and presence of EMRL, respectively. We noted that I_{corr} and I'_{corr} was calculated from the intersection of the cathodic and anodic Tafel lines.

From this figure, it can be seen that, with the increase of the extract concentrations, both anodic and cathodic currents were inhibited. This result shows that the addition of the *Mentha rotundifolia* inhibitor reduced anodic dissolution and also retarded the hydrogen evolution reaction.

In addition, the parallel cathodic Tafel curves in Fig. 1 show that the hydrogen evolution is activation controlled, and the reduction mechanism is not affected by the presence of the inhibitor [39]. The inspection of results in Table 2 indicate that

the *EMRL* inhibits the corrosion process in the studied range of concentrations and E (%) increases with the concentration of the inhibitor, reaching its maximum value, 92.9 %, at 35 %. The values of the cathodic Tafel lines, bc, show slight changes with the addition of *EMRL*. This result means that the mechanism at the electrode reaction is not changed [40]. The free corrosion potential determined after 30 mn of immersion does not change in the presence of the inhibitor; thus, it can be classified as a mixed-type inhibitor in 1 M HCl.

Electrochemical impedance spectroscopy measurements

The corrosion behavior of steel, in acidic solution with and without *EMRL*, was also investigated by EIS measurements at 298 K (Fig. 2).

The electrochemical impedance parameters derived from these investigations are mentioned in Table 3.

The inhibition efficiency obtained from the charge transfer resistance is calculated by:

$$E_{Rt} \% = \frac{(R_t - R_t^0)}{R_t} \times 100 \quad (3)$$

where R_t and R_t^0 are the charge transfer resistances in inhibited and uninhibited solutions, respectively.

The charge transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [41]. The double layer capacitance (C_{dl}) values were obtained at maximum frequency (f_{max}), at which the imaginary component of the Nyquist plot is maximum and calculated using the following equation:

Fig. 2 Nyquist diagrams for steel electrode with and without *EMRL* at 298 K after 30 min of immersion

Table 3 Impedance parameters for corrosion of steel in 1 M HCl in the absence and presence of different concentrations of EMRL at 298 K

Inhibitor	C (%)	R_t (Ω cm ²)	$f_{\max}$ (Hz)	C_{dl} (μ F/cm ²)	E_{Rt} (%)
Blank	0	62.63	25.82	98.46	–
Extract of <i>Mentha rotundifolia</i> leaves	1	121.61	45.39	28.84	48.5
	3	157.40	43.07	23.48	60.2
	5	214.61	79.80	9.29	70.8
	10	275.50	90.25	6.40	77.3
	20	334.79	85.27	5.57	81.8
	35	456	144.23	2.42	86.3

$$C_{dl} = \frac{1}{2 \cdot \pi \cdot f_m \cdot R_t} \quad (4)$$

with C_{dl} is the double layer capacitance (μ F cm⁻²), $f_{\max}$ is the maximum frequency (Hz), and R_t is the charge transfer resistance (Ω cm²).

From Table 3, it is clear that the R_t values increased and that the C_{dl} values decreased with increasing inhibitor concentration. These results indicate a decrease in the active surface area caused by the adsorption of the inhibitors on the steel surface, and it suggests that the corrosion process became hindered. The best result for the inhibition efficiency of the extract of *Mentha rotundifolia* leaves were obtained at a concentration of 35 %, with efficiency equal to 86.3 %. We also notice that the results obtained from weight loss are in good agreement with the electrochemical studies.

Effect of temperature on corrosion inhibition

The effect of temperature on the corrosion rate of steel in 1 M HCl containing inhibitor at a maximal concentration (35 %) was studied in the temperature range 298–338 K using weight loss measurements during 1 h, the corresponding results are summarized in Table 4. The results suggest that the extract was adsorbed on the steel surface at all temperatures studied.

The data in Table 4 indicate that the rates of steel corrosion in the absence and presence of the extract increased with the rise in temperature in acid media. This is because an increase in temperature usually accelerates corrosive processes, particularly in media in which H₂ gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal.

Table 4 Effect of temperature on the steel corrosion in the presence and absence of 35 % of leaves extract at 1 h

T (K)	W_0 (mg/cm ² h)	W (mg/cm ² h)	E (%)
298	0.1693	0.0265	84.3
308	0.3381	0.0626	81.5
318	1.1464	0.1236	89.2
328	4.0315	0.2472	93.8
338	12.391	0.3625	97.1

Fig. 3 Variation of E (%) with 35 % of EMRL at different temperatures in 1 M HCl

The plots in Fig. 3 show that inhibition efficiency generally increased with the rise in temperature.

Figure 4 also shows that the corrosion reaction can be regarded as an Arrhenius-type process (Eq. 5). The activation parameters for the studied system (E_a , ΔH_a^* and ΔS_a^*) were estimated from the Arrhenius equation and transition state equation (Eq. 6):

$$W = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (5)$$

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^*}{R}\right) \exp\left(-\frac{\Delta H_a^*}{RT}\right) \quad (6)$$

where A is Arrhenius factor, E_a is the apparent activation corrosion energy, N is the Avogadro's number, h is the Plank's constant, and ΔH_a^* and ΔS_a^* are the enthalpy and the entropy changes of activation corrosion energies for the transition state complex, respectively. R is the perfect gas constant.

The apparent activation energy was determined from the slopes of $\ln W$ versus $1,000/T$ graph depicted in Fig. 4.

Figure 5 shows a plot of $\ln (W/T)$ against $1/T$ of the extract. Straight lines are obtained with a slope of $(-\Delta H_a^*/R)$ and an intercept of $(\ln R/Nh + \Delta S_a^*/R)$ from which the values of ΔH_a^* and ΔS_a^* are calculated, respectively (Table 5).

From the following results, it can be concluded that:

- The activation energy decreased in the presence of the inhibitor studied.
 - The E_a and ΔH_a^* values vary in the same way with the inhibitor concentration.
- This result permits the verification of the known thermodynamic relationship between E_a and ΔH_a^* [42]:

$$E_a - \Delta H_a^* = RT \quad (7)$$

The calculated values are very close to RT which equals 2.64 kJ mol^{-1} at 318 K.

- The positive values of ΔH_a^* show that the corrosion process is an endothermic phenomenon.

Fig. 4 Arrhenius plots of $\ln W$ versus $1,000/T$ without and with 35 % of *EMRL*

Fig. 5 $\ln W/T$ versus $1/T$ for steel dissolution in 1 M HCl in the absence and presence of 35 % of *EMRL*

Table 5 The values of E_a , ΔH_a^* and ΔS_a^* for steel in 1 M HCl in the absence and the presence of 35 % of *EMRL*

Inhibitor	E_a (kJ/mol)	ΔH_a^* (kJ/mol)	ΔS_a^* (J/mol)	$E_a - \Delta H_a^*$ (kJ/mol)
Blank	92.41	89.77	376.62	2.64
35 % of <i>EMRL</i>	55.55	52.92	244.07	2.63

- The value of E_a in the presence of *EMRL* is lower than that of the white. We remark that the addition of inhibitor modified the values of E_a ; this modification may be attributed to the change in the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [43, 44]. The lower value of the activation energy of the process in an inhibitor's presence when compared to that in its absence is attributed to its chemisorption [2, 27, 45].

- The decrease of values of ΔS_a^* show that the activated complex in the rate-determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [46].

Adsorption considerations

The effectiveness of organic compounds as corrosion inhibitors can be ascribed to the adsorption of molecules of the inhibitors through their polar functions on the metal surface. Some authors [47, 48] have pointed out that adsorption on corroding surfaces never reaches the real equilibrium and tends to an adsorption steady state. However, when the corrosion rate is sufficiently small, the adsorption steady has a tendency to become a quasi-equilibrium state. Therefore, it is reasonable to consider the quasi-equilibrium adsorption in a thermodynamic manner using the appropriate equilibrium isotherms. Adsorption isotherms provide information about the interaction among adsorbed molecules themselves as well as their interactions with the metal surface. Surface coverage values were evaluated from the gravimetric measurements assuming a direct relationship between inhibition efficiency and surface coverage. The surface coverage values were fitted to different adsorption isotherm models and the best results judged by the correlation coefficient (R^2) were obtained with the Langmuir adsorption isotherm.

The Langmuir isotherm is given by the expression:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (8)$$

where θ is the surface coverage, C is the concentration, and K_{ads} is the equilibrium constant of adsorption process. The plot of C/θ against C is shown in Fig. 6. Linear plots were obtained with a very good correlation coefficient (0.996) which seems to suggest that adsorption of the extract is by the Langmuir adsorption isotherm.

The considerable observed deviation of the slope from unity (1.159) may be explained on the basis of the interaction among the adsorbed species on the surface of the metal [49]. Given the complex composition of the extract, different components can be adsorbed on the cathodic and anodic sites of the metal surface, and such adsorbed species may interact by mutual repulsion or attraction. It is therefore pertinent to say that the adsorption of the extract on the steel surface at this temperature can be more appropriately represented by a modified Langmuir equation suggested by Villamil et al. [50], taking into consideration the interactions between adsorbate species as well as changes in the heat of adsorption with changing surface coverage as follows:

$$\frac{C}{\theta} = \frac{n}{K_{\text{ads}}} + nC \quad (9)$$

It is pointed out that the inhibition by natural plants is due to the synergistic effect of the various components of the extract or oil [51–53].

Fig. 6 Langmuir isotherm plot for *EMRL* at 298 K

Conclusion

From the overall experimental results following conclusions can be deduced:

1. The *EMRL* acts as a good inhibitor for the corrosion of steel in 1 M HCl.
2. The inhibition efficiency of *EMRL* increases with the concentration to attain a maximum value 92.87 % at 35 %.
3. The *EMRL* acts as mixed inhibitor without modifying the hydrogen reduction mechanism.
4. The inhibition efficiency of *EMRL* increases with the rise of temperature.
5. The *EMRL* studied was adsorbed chemically on the steel surface according to the Langmuir isotherm model.
6. The inhibition efficiencies of the tested inhibitors obtained from the polarization technique are in good agreement, within 2 %, with the values obtained from the gravimetric measurements. This agreement among two independent techniques proves the validity of the results.

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