

Corrosion Inhibition of Carbon Steel in 1 M Sulphuric Acid Solution by Extract of *Eucalyptus globulus* Leaves Cultivated in Tunisia Arid Zones

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Received: 4 February 2015 / Revised: 4 May 2015 / Accepted: 5 May 2015 / Published online: 16 May 2015
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Abstract The corrosion inhibition effect of the methanolic extract of *Eucalyptus globulus* leaves as an eco-friendly green inhibitor for corrosion control of carbon steel in 1 M H₂SO₄ solution was studied using weight loss measurements and different electrochemical methods. It was found that *E. globulus* extract acts as a strong inhibitor. Results showed that this compound acts as a mixed-type inhibitor. As the inhibitor concentration increased, the charge transfer resistance of carbon steel increased and double layer capacitance decreased. The results of weight loss measurements were in good agreement with other electrochemical methods results. It was found that this green inhibitor acts through adsorption on the metal surface. In addition, adsorption obeys the Langmuir isotherm.

Keywords *Eucalyptus globulus* · Carbon steel · Eco-friendly inhibitor · Electrochemical methods

1 Introduction

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric and sulphuric acids are widely used in the pickling processes of metals [1]. The use of inhibitors is

one of the best methods of protecting metals against corrosion [2, 3].

Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen in their functional groups with aromatic and heterocyclic rings [4–20]. These organic compounds can be absorbed on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate. Most of investigated compounds are toxic and cause severe environmental hazards.

Some investigations have in recent times been made into the corrosion inhibiting properties of natural products of plant origin, and some natural products have been found to generally exhibit good inhibition efficiencies [21–35]. The significance of this area of research is primarily due to the fact that natural products are environmentally friendly and ecologically acceptable. The yield of these natural products as well as the corrosion inhibition abilities of the plant extracts vary widely depending on the part of the plant [33, 35, 36] and its location [37]. One compound effective in a certain medium with a given metal may be ineffective for the same metal in another medium [31].

The use of natural products as corrosion inhibitors have been widely reported by several authors. The corrosion inhibition activity of plant extracts could be due to the presence of heterocyclic constituents like alkaloids, flavonoids, etc., even the presence of tannins, cellulose and polycyclic compounds normally enhances the film formation over the metal surface, thus aiding corrosion.

The aim of this paper is to extract and to test methanolic extract of *Eucalyptus globulus* (*E. globulus*) as corrosion inhibitor for steel in 1 M H₂SO₄ solution. The study is conducted by weight loss, polarisation curves, and electrochemical impedance spectroscopy methods. *E. globulus* belongs to *Myrtaceae* family and contains 1'Eucalyptol (1,8-cineole) [38].

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2 Materials and Methods

2.1 Inhibitor Preparation

Eucalyptus globulus (*E. globulus*) plant was collected in March, 2012 in the region of Medenine, Tunisia. *E. globulus* leaves were air dried 30 days in the laboratory at room temperature, before using them for the preparation of the extract. The extraction was performed by the soxhlet technique for 6 h with the methanol as solvent of extraction. The extracted solution was concentrated until extract solidification. This solid extract was used to study the corrosion inhibition. It was dissolved in 1 M H₂SO₄ at different concentrations ranging from 0.5 to 1.5 g L⁻¹ [39]. The test solutions are freshly prepared before each experiment.

2.2 Specimen Preparation

Corrosion tests were performed on a carbon steel of the following percentage composition (wt%): Fe 99.52 %, C 0.22 %, Si 0.024 %, Mn 0.089 %, S 0.004 %, Ni 0.014 %, Cr 0.009 %, Al 0.034 %, V 0.016 %, Ti 0.003 %, Cu 0.022 % and P 0.046 %, which were abraded successively with fine grade emery papers of 120 to 1200 grade. The specimens were washed thoroughly with double distilled water and finally degreased with acetone and dried at room temperature.

2.3 Electrolyte

The aggressive solution (1 M H₂SO₄) is prepared by dilution of analytical grade 98 % H₂SO₄ with bidistilled water in the absence and presence of the green inhibitor in the concentration range of 0.5 to 1.5 g L⁻¹.

2.4 Weight Loss Method

Weight loss measurements were performed on the carbon steel samples in a rectangular form of size 7 × 3 × 0.5 cm in 1 M H₂SO₄ solution in the presence and absence of different concentrations of *E. globulus* extract. Every sample was weighed by an electronic balance, and then placed in the acid solution (150 mL). The duration of the immersion was 90 days at the ambient temperature. After immersion, the surface of the specimen was chemically cleaned according to the standard procedure ASTM G1-90 (reapproved 1999) [40], and the sample was weighed again in order to calculate the inhibition efficiency (IE_w %) and the corrosion rate (CR_w). The experiments were performed in triplicate and the average value of the weight loss was noted. For each experiment, a freshly prepared solution was used.

$$\text{IE}_w(\%) = \frac{w_0 - w_1}{w_0} \times 100, \quad (1)$$

where w_i and w_0 are the weight loss values in the presence and absence of the green inhibitor, respectively.

The corrosion rate (CR_w) of mild steel was calculated using the relation:

$$\text{CR}_w = \frac{87.6 \times \Delta w}{Atd} \text{ (mm year}^{-1}\text{)}, \quad (2)$$

where Δw is the weight loss of carbon steel (mg), A is the area of the coupon (cm²), t the exposure time (h), and d is the density of carbon steel (g cm⁻³).

2.5 Electrochemical Studies

For Tafel polarisation and A.C. impedance studies, carbon steel specimens embedded in resin with an exposed cross-sectional area of 0.29 cm² were used as the working electrode. The specimens were polished with a sequence of emery papers of various grades (120–1200) washed with double distilled water before usage and finally dried by warm air. These cleaned specimens were kept in desiccators until the time of experiment. Platinum and a standard calomel electrode (SCE) were employed as counter and reference electrodes, respectively. Thus all potentials reported are referred to SCE. The experimental temperature was 25 ± 1 °C.

The polarisation and A.C. impedance experiments were carried out by a PGSTAT consisting of a model AUTOLAB.

Tafel polarisation sweep was conducted in the potential range ±0.25 mV versus open circuit potential (O.C.P.) at a scan rate of 1 mV s⁻¹, the potential was stabilized at free potential during 10 min.

The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (j_{corr}). The inhibition efficiency (IE_j %) was evaluated from the measured j_{corr} values using the relationship:

$$\text{IE}_j(\%) = \frac{j_{\text{corr}}^0 - j_{\text{corr}}^{\text{inh}}}{j_{\text{corr}}^0} \times 100, \quad (3)$$

where j_{corr}^0 and $j_{\text{corr}}^{\text{inh}}$ are the corrosion current in the absence and in the presence of the green inhibitor, respectively.

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out over a frequency range of 100 kHz to 10 mHz with five points per decade; a sine wave with 10 mV amplitude was used to perturb the system. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

The charge transfer resistance values (R_t) were obtained from the diameter of the semicircles of the Nyquist plots.

The inhibition efficiency ($IE_{EIS} \%$) of the inhibitor has been found from the charge transfer resistance values using the following equation:

$$IE_{EIS} (\%) = \frac{R_t^{inh} - R_t^0}{R_t^{inh}} \times 100 \quad (4)$$

where R_t^0 and R_t^{inh} are the charge transfer resistance in the absence and in the presence of the green inhibitor, respectively. All electrochemical measurements were done in unstirred and non de-aerated solutions.

3 Results and Discussions

3.1 Weight Loss Studies

Figure 1 represents the effect of *E. globulus* extract concentration on inhibition efficiency in 1 M H_2SO_4 . The results collected show that the methanolic extract inhibited the corrosion of carbon steel in 1 M H_2SO_4 solutions. The corrosion rate was found depending on the inhibitor concentrations. The increase in the methanolic extract concentration increases the inhibition efficiency $IE_w \%$ to about 85 % at 1.5 g L^{-1} . The inhibitory action of natural compounds against steel corrosion can be attributed to the component adsorption on the metal surface. This adsorption limits the dissolution of metal by blocking its corrosion sites and hence decreasing the weight loss with the increasing efficiency as the concentration increases.

3.2 Polarisation Curves

Polarisation curves for carbon steel in 1 M H_2SO_4 in the absence and presence of *E. globulus* leaves extract at various concentrations are shown in Fig. 2.

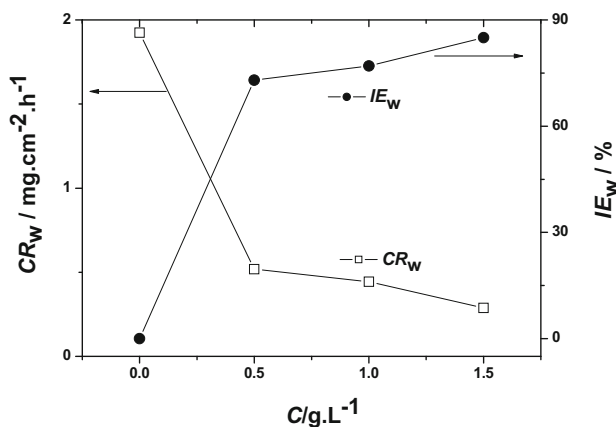


Fig. 1 Variation of corrosion rate and inhibition efficiency of carbon steel in 1 M H_2SO_4 in the absence and presence of *E. globulus* methanolic extract

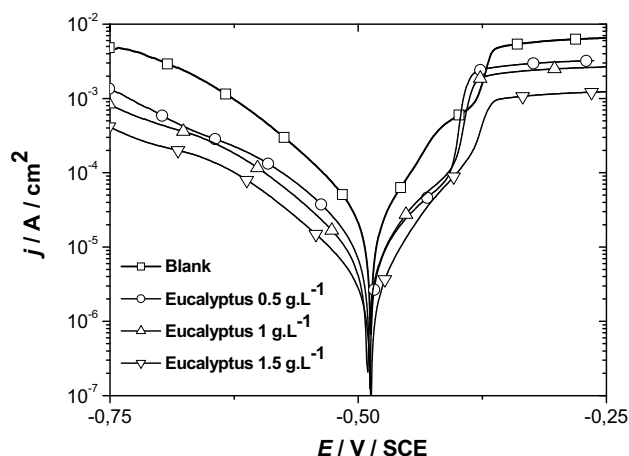


Fig. 2 Polarisation curves for carbon steel in 1 M H_2SO_4 in the absence and presence of different concentrations of *E. globulus* inhibitor

Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (j_{corr}) and cathodic and anodic tafel slopes (b_c , b_a) were determined using the Stern and Geary equation in the Tafel regions (near E_{corr}) (Table 1). The inhibition efficiency ($IE_j \%$) was calculated from the relationship (Eq. 3) (Table 1).

According to Stern and Geary [41], one can express the current density j near the open-circuit potential by

$$j = j_{corr} \{ \exp[b_a(E - E_{corr})] - \exp[b_c(E - E_{corr})] \}. \quad (5)$$

Figure 3 shows an example of the calculation results by nonlinear regression using the Stern and Geary equation.

The result obtained by applying this equation shows a good concordance with the experimental results.

The nominal corrosion rate in terms of corrosion penetration ($\mu\text{m year}^{-1}$) can be calculated using Faraday's law as [42]

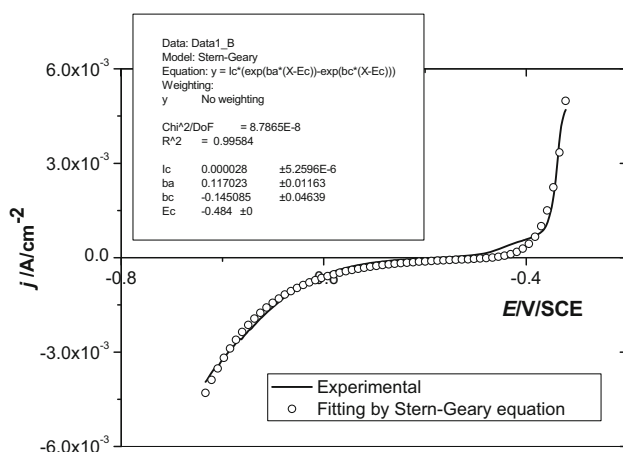
$$CR_j = \frac{Ka_w}{nFd} j_{corr} = \alpha j_{corr}, \quad (6)$$

where $K = 315,360$ is a units conversion factor, F is the faraday constant ($F = 96,485 \text{ C mol}^{-1}$), n is the number of moles of electrons transferred, a_w is the atomic weight in grams, d is the density of the metal in g cm^{-3} and j_{corr} is the corrosion current density in $\mu\text{A cm}^{-2}$. The value of the constant α for steel is approximately $\alpha_{Fe} = 11.6 \mu\text{A}^{-1} \text{ cm}^2 \mu\text{m year}^{-1}$.

From the Table 1, it is clear that corrosion potential (E_{corr}) did not change after the addition of the methanolic extract at various concentrations. The change in β_a and β_c values as shown in Table 1 indicates that the addition of *E. globulus* extract modifies the mechanism of anodic dissolution as well as cathodic hydrogen evolution. But, in the present situation, it is very difficult to decide whether it is the cathodic reaction which is predominantly retarded or the anodic reaction.

Table 1 Polarisation parameters for carbon steel in 1 M H₂SO₄ in the absence and presence of *E. globulus* extract at various concentrations

C (g L ⁻¹)	E (mV ECS ⁻¹)	j _{corr} (μA cm ⁻²)	β _a (mV dec ⁻¹)	β _c (mV dec ⁻¹)	IE _j %	CR _j (μm year ⁻¹)
(Blank) 0	-0.484	28.6	117	145	-	331.7
0.5	-0.482	8.2	85	98	71.3	95.1
1.0	-0.491	7.5	80	94	73.7	87.0
1.5	-0.490	4.1	73	82	85.6	47.6

**Fig. 3** Experimental and calculated j - E curves to evaluate the electrochemical parameters (circle) experimental data; (solid line) calculated data

This result indicated that the methanolic extract can be classified as mixed-type inhibitor in 1 M H₂SO₄ solution.

It is illustrated from the data of Table 1 that the addition of Eucalyptus extract decreases the corrosion current density. The decrease in j_{corr} values can be due to the adsorption of the methanolic extract on the carbon steel surface. This idea was investigated in a separate section by plotting a suitable adsorption isotherm. Moreover, it can be clearly seen that the inhibition efficiency of the methanolic extract increases with the inhibitor concentration. This behaviour shows that *E. globulus* extract acts as a good inhibitor for the corrosion of carbon steel in 1 M H₂SO₄ media.

The presence of the methanolic extract of *E. globulus* at a concentration of 1.5 g L⁻¹ in the acidic medium (1 M H₂SO₄) reduced the corrosion rate ($\approx 47 \mu\text{m year}^{-1}$). However, this inhibitor does not completely prevent corrosion.

3.3 EIS Measurements

The corrosion behaviour of carbon steel in 1 M H₂SO₄ solution in the absence and presence of *E. globulus* leaves extract was investigated by EIS at $25 \pm 1^\circ\text{C}$ after 10 min of immersion. Surface properties, electrode kinetics and mechanistic information can be obtained from the impedance diagrams [43–46].

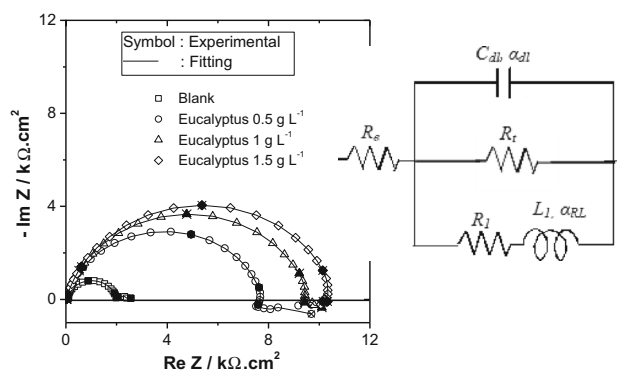
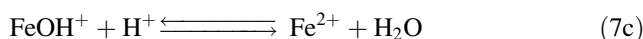
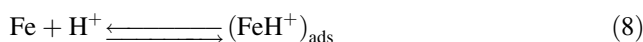
**Fig. 4** Nyquist plot of carbon steel in 1 M H₂SO₄ solution in the absence and presence of different concentrations of *E. globulus* inhibitor at 298 K (experimental measurement) and fitted results using equivalent circuit model, (1RC-1RL)

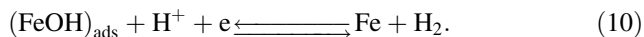
Figure 4 shows the results of EIS experiments in the Nyquist representation. After analysing the shape of the Nyquist plots, it is concluded that the Nyquist plots showed a depressed capacitive loop in the high-frequency (HF) range and small inductive loop in the low-frequency (LF) range indicating the occurrence of a Faradic process on free electrode sites. The HF capacitive loop can be attributed to the charge transfer reaction and time constant of the electric double layer. On the other hand, the LF inductive loop may be attributed to the relaxation of intermediates controlling the anodic process resulting from adsorption species such as FeSO₄ [47], or inhibitor species [48, 49] on the electrode surface. It might also be attributed to the redissolution of the passivated surface at LF [50].

Bockris et al. [51] proposed that Fe electro-dissolution in acidic sulphate solutions depends primarily on the adsorbed intermediate FeOH_{ads} as follows:



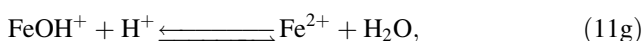
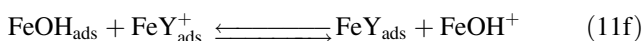
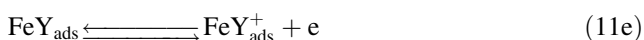
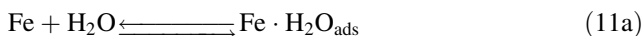
The cathodic hydrogen evolution follows the steps:





The corrosion rate of iron in H₂SO₄ solutions is controlled by both hydrogen evolution reaction and dissolution reaction of iron.

Another mechanism involving two adsorbed intermediates has been used to account for the retardation of Fe anodic dissolution in the presence of an inhibitor [52]:



where Y represents the inhibitor species.

The EIS spectra are simulated by the equivalent circuit shown in Fig. 4.

The equivalent circuit consists of the double layer capacitance (*C_{dl}*) in parallel to the charge transfer resistance (*R_t*), which is in parallel to the series of inductive elements *L₁* and *R_L*. The presence of *L* in the impedance spectra in the presence of the inhibitor indicates that steel is always dissolved by the direct charge transfer at the *E. globulus* adsorbed in the steel surface [53]. The results of regression calculations with a simplex method for this system are overlaid on Fig. 4. The comparison of experimental and calculated spectra corroborates the adequacy of the equivalent circuit adopted.

The impedance parameters such as charge transfer resistance (*R_t*; diameter of high frequency loop), derived double layer capacitance (*C_{dl}*) and inhibition efficiency (*IE_{EIS}* %) are listed in Table 2.

The values of the double layer capacitance were obtained at maximum frequency (*f_m*), at which the imaginary

component of the Nyquist plot is maximal, and calculated using the following equation:

$$C_{dl} = \frac{1}{2\pi f_m R_t} \tag{12}$$

where *C_{dl}* is the double layer capacitance (μF cm⁻²), *f_m* is the maximum frequency (Hz) and *R_t* is the charge transfer resistance (Ω cm²).

The diameter of the capacitive loop in the presence of inhibitor is larger than that in the absence of inhibitor and increases with the inhibitor concentration. This indicates that the impedance of inhibited substrate increases with the inhibitor concentration.

The existence of the capacitive loops and disappearance of the low-frequency inductive loops when compared with the Nyquist diagram in the 1 M H₂SO₄ solutions without inhibitors and in the presence of *E. globulus* extract could be related to the gradual replacement of water molecules and/or hydroxyl ions by organic inhibitors on the surface of the metal.

It is apparent that as the concentration of the methanolic extract increased, the *R_t* values increased indicating decrease in the formation of intermediates that control the anodic process from metal dissolution and subsequently inhibition of corrosion. The increase of charge transfer resistance with the inhibitor concentration suggests that more inhibitor molecules are adsorbed on the metal surface at higher concentration leading to a greater surface coverage. The decrease in the capacity was caused by reduction in local dielectric constant and/or by increase in the thickness of the electrical double layer. This fact suggests that the inhibitor molecules act by adsorption at the metal/solution interface [54–58].

From Table 2, it is clear that the greatest effect was observed at 1.5 g L⁻¹ of *E. globulus* extract which gives *R_t* value of 10,272 and 1640 Ω cm² in 1 M H₂SO₄.

The data obtained from EIS are in good agreement with those obtained from polarisation curves method. It is concluded that the corrosion rate depends on the chemical nature of the electrolyte rather than the applied technique.

3.4 Adsorption Isotherm

Inhibition effects are based on the adsorption of molecules onto the metal surface to form an impermeable protective film and shielding it from the corrosive media. On the other hand, the adsorbed molecules can combine with the oxide layer on the metal (rust deposited) and react chemically to produce a more protective surface network by changing the film structure. The adsorption mechanism of organic compounds occurs either directly, on the basis of donor–acceptor interactions between the relatively loosely bound electrons such as in anions and organic molecules and/or

Table 2 Impedance parameters for carbon steel in 1 M H₂SO₄ solution in the absence and presence of *E. globulus* extract at various concentrations

<i>C</i> (g L ⁻¹)	<i>R_t</i> (Ω cm ²)	<i>C_{dl}</i> (μF cm ⁻²)	<i>IE_{EIS}</i> %
(Blank) 0	1640	150	–
0.5	7640	93	78.5
1.0	9420	78	82.6
1.5	10,272	52	84.1

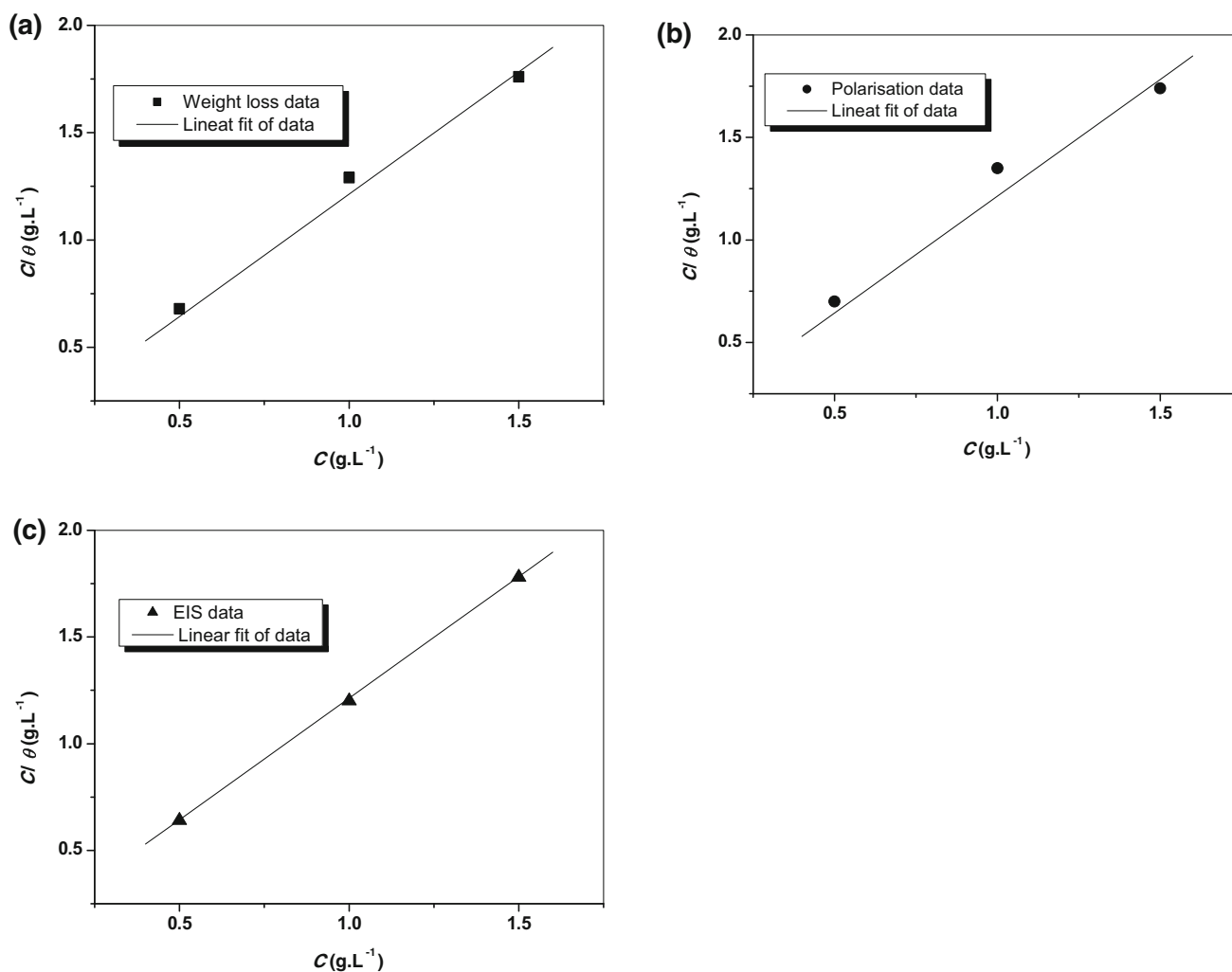


Fig. 5 Langmuir isotherm for the adsorption of *E. globulus* methanolic extract on the carbon steel surface: **a** (weight loss data), **b** (polarisation data) and **c** (EIS data)

the heterocyclic compound which has lone pair electrons, or the π -electrons with the vacant d-orbitals of metallic iron atoms. Some parameters such as organic molecule size, number of functional groups, polarity that contribute to the formation of a strong bond or the rate of adsorption of inhibitor compounds onto the surface could affect the adsorption mechanism or inhibition action [59].

The Langmuir adsorption isotherm provides a simple mechanistic picture of the adsorption process and gives rise to a relatively simple mathematical expression. The Langmuir adsorption isotherm may be written in the following rearranged form [60]:

$$KC = \frac{\theta}{1 - \theta}. \quad (13)$$

Here K is the equilibrium constant. It is convenient to rearrange the equation, yielding

$$\frac{C}{\theta} = C + \frac{1}{K}, \quad (14)$$

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant, θ is the surface coverage.

The surface coverage, θ , was determined using the following equations:

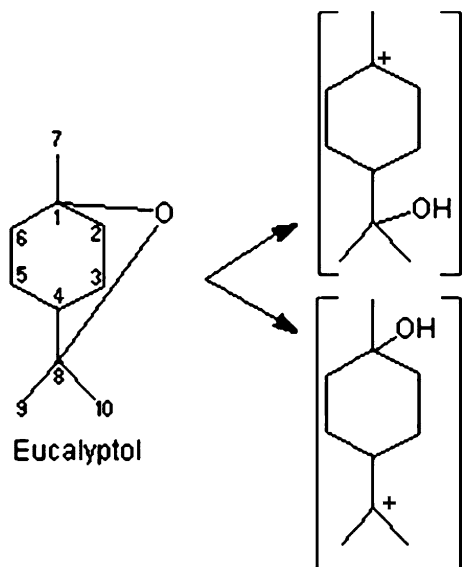
$$\theta = \frac{\text{IE}\%}{100}. \quad (15)$$

For all the three methods used in this study (weight loss, polarisation, and EIS), a plot of C/θ against C gave straight lines with the slope of unit (Fig. 5). This means that the adsorption of the methanolic extract on the carbon steel surface obeys the Langmuir isotherm.

The free energy of adsorption (ΔG_{ads}) was calculated using the results of different methods through the following equation [61]:

Table 3 The values of free Gibbs energy of adsorption calculated using the results of different electrochemical studies

Method	Weight loss	Polarisation	EIS
ΔG_{ads} (kJ g ⁻¹)	-13.55	-13.38	-14.04

**Fig. 6** Protonation of eucalyptol in acidic medium

$$\Delta G_{\text{ads}} = -RT \ln(55.5K) \quad (16)$$

The calculated values are given in Table 3. The values of ΔG_{ads} from the different methods used were in good agreement with each other. ΔG_{ads} values are around -13 kJ g^{-1} ($-13 \times M$, kJ mol^{-1}). Although the molecular weight of extract was not determined, ΔG_{ads} value was given in kJ g^{-1} unit. The negative values of ΔG_{ads} are an indication of the spontaneous adsorption of inhibitor on the surface of the carbon steel [60].

In general, values of ΔG_{ads} up to -20 kJ mol^{-1} were consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption). On the other hand, negative values less than -40 kJ mol^{-1} involved sharing or transferring of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [62].

In this study, the calculated ΔG_{ads} values greater than -40 kJ mol^{-1} indicate that the adsorption mechanism of the investigated inhibitor on carbon steel in 1 M H_2SO_4 solution is typical of chemisorption [62]. However, the methanolic extract of *E. globulus* contains Eucalyptol (1,8-cineole). The latter can be easily protonated in the sulphuric acid solution because the molecule contains O atoms with lone pair electrons and π -electrons. Thus, they

become cations, existing in equilibrium with the corresponding molecular form (Fig. 6).

Therefore, physical adsorption may take place due to electrostatic interaction between the protonated molecule and FeSO_4^{2-} species.

4 Conclusions

Based on the results of investigation, the following conclusions are drawn:

- Methanolic extract of *E. globulus* is a good eco-friendly green inhibitor for carbon steel in 1 M H_2SO_4 solutions and can be used to replace toxic chemicals.
- Inhibition efficiency value increases with the inhibitor concentration; the maximum inhibition efficiency was 84 %.
- Polarisation studies showed that *E. globulus* is a mixed-type inhibitor in 1 M H_2SO_4 .
- EIS plots indicated that the charge transfer resistances increase with the increasing concentration of the extract.
- The data obtained from the three different methods—potentiodynamic polarisation, EIS and weight loss, are in good agreements.
- The corrosion inhibition was probably due to the adsorption of the green inhibitor on the metal surface without changing the mechanism of partial corrosion reaction and blocking its active sites.
- The data obtained from this study were fitted well into the Langmuir adsorption isotherm. Adsorption of the studied bio-inhibitor on the carbon steel surface in 1 M H_2SO_4 represented a mixture of physical and chemical adsorption.

Conflict of interest On behalf of all authors, Naceur Ettayeb states that there is no conflict of interest.

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