Int. J. Electrochem. Sci., 8 **(2013)** 4328 - 4345

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Evaluation of *Eryngium maritimum* Essential Oil as Environmentally Friendly Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution

F. Darriet[1], *M. Znini*[2], *L. Majidi*[2,*], *A. Muselli*[1], *B. Hammouti*[3], *A. Bouyanzer*[3], *J. Costa*[1]

[1]Université de Corse, UMR CNRS 6134, Laboratoire de Chimie des Produits Naturels, Faculté des Sciences et Techniques, Corse, France.
[2]Université My Ismail, Laboratoire des Substances Naturelles & Synthèse et Dynamique Moléculaire, Faculté des Sciences et Techniques, Errachidia, Morocco.
[3]LCAE-URAC18, Faculté des Sciences, Université Mohamed Premier, Oujda, Morocco.
[*]E-mail: lmajidi@yahoo.fr

Received: 10 January 2013 / *Accepted:* 19 February 2013 / *Published:* 1 March 2013

Essential oil of aerial parts of *Eryngium maritimum* L. (EM oil) was obtained by hydrodistillation and analyzed by GC and GC/MS. After column chromatography (CC), 58 compounds accounting for 97.1 % of the oil were identified. The essential oil was dominated by oxygenated sesquiterpenes (57.9 %). The main components were 4βH-cadin-9-en-15-al (36.5 %), germacrene D (31.6 %), 4βH-cadin-9-en-15-ol (8.3 %) and 4βH-muurol-9-en-15-al (6.5 %). The inhibition of the corrosion of mild steel in 1M HCl solution by *EM* oil and its CC-fractions have been studied using weight loss measurements. Inhibition was found to increase with increasing concentration of the essential oil to attain 97.91 % at 2 mg/mL. The effect of temperature on the corrosion behavior of mild steel in 1M HCl without and with the *EM* oil at 2 mg/mL was also studied. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the mild steel surface according to the Langmuir adsorption isotherm. The thermodynamic parameters for activation and adsorption processes were calculated and discussed. The results obtained showed that the *EM* oil could serve as an environmentally friendly inhibitor of the corrosion of mild steel in HCl media.

Keywords: Adsorption, Corrosion Inhibition, Essential oil, Mild steel, *Eryngium maritimum* L.

1. INTRODUCTION

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric acid was widely used in the pickling processes of metals [1]. The use of inhibitors is one of the best methods of protecting metals against corrosion in acid treatment solutions [2]. Most corrosion inhibitors are organic compounds having hetero atoms in their aromatic or long carbon chain [3]. These organic compounds can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate. However, the toxic effects of most synthetic corrosion inhibitors, the obligations of health and human security have led to the research of green alternatives that are environmentally friendly and harmless [2,3].

Recently the researches have been focused on the use of eco-friendly compounds and ecologically acceptable such as essential oils, extract of common plants, because to bio-degrability, eco-friendliness, low cost and easy availability and renewable sources of materials [4]. In this context, in our laboratory, much work has been conducted to study the inhibition by some essential oils on the corrosion of steel in acidic media. It has been reported that the essential oils of *Salvia aucheri* var. *mesatlantica* [5], *Mentha spicata* [6], *Warionia saharea* [7], *Lavandula multifida* [8], *Pulicaria mauritanica* [9], *Asteriscus graveolens* [10] *and Helichrysum italicum* subsp. *italicum* [11] have been found to be very efficient corrosion inhibitors for mild steel in HCl and H_2SO_4 media. In order to extend the earlier work, essential oil of *Eryngium maritimum* L is chosen to use as the corrosion inhibitor on mild steel in 1M HCl media.

The genus *Eryngium* belongs to the *Apiaceae* family and includes around 250 species that are widespread throughout the world [12]. Among them, several *Eryngium* species have been used as ornamental plants, condiments [13] or in traditional medicine [14,15]. *Eryngium maritimum* L. usually named “Sea holly” in England or “Panicaut des mers” in France, is a perennial plant (30-60 cm high) with mauve flowers (blossoming time June–September), growing wild on the sandy beaches of West Europe, Mediterranean basin and Black Sea [12]. The plant is one of the typical dune species implicated in the plant network that contributes to sand dune edification and restoration [16,17]. *E. maritimum* have also been reported to exhibit different therapeutic uses in folk medicine as diuretic or hypoglycemic [18]. In our previous studies [19], Germacrene-D and three uncommon oxygenated sesquiterpenes: 4βH-cadin-9-en-15-al, 4βH-cadin-9-en-15-ol and 4βH-muurol-9-en-15-al were reported as major component of *E. maritimum* essential oil from Corsica.

The aim of the present work is to study the inhibitive action of *E. maritimum* essential oil, its CC-fractions and more precisely the anticorrosive action of uncommon oxygenated sesquiterpenes 4βH-cadin-9-en-15-al, 4βH-cadin-9-en-15-ol, 4βH-muurol-9-en-15-al and 4βH-muurol-9-en-15-ol of mild steel in 1M HCl solution using weight loss measurements. In this case, the effect of concentration and temperature on the inhibition efficiency has been examined. The thermodynamic parameters for activation and adsorption processes were calculated and discussed.

2. EXPERIMENTAL PART

2.1. Plant material

The aerial parts of *E. maritimum* were harvested in June 2012 (full bloom) on sand beach of Quercionu in Corsica Island (France). Voucher specimens of plants from each location were deposited in the herbarium of University of Corsica, Corte, France.

2.2. Essential oil isolation

Fresh aerial parts of *E. maritimum* were hydro-distilled during five hours using a Clevenger type apparatus in accordance with the method recommended in the European Pharmacopoeia [19]. The yield of essential oil calculated from fresh plant material was 0.089%.

2.3. Oil fractionation

The essential oil of *E. maritimum* (10 g) was separated by an automatized flash chromatography (AFC) system (*TeledyneEIsco,* Lincoln) using normal-phase silica (40g, 15-40μ, 60Å). The hydrocarbon (**HF**) and oxygenated (**OF**) fractions were eluted with hexane and iPr_2O, respectively (Fig. 1). Two oxygenated sub-fractions (**OF 1** and **OF 2**) were eluted with a mixture of iPr_2O/hexane % iPr_2O/hexane (time) were: 3% (7 min) and 100% (10 min). The experimental conditions were reported in Fig. 1.

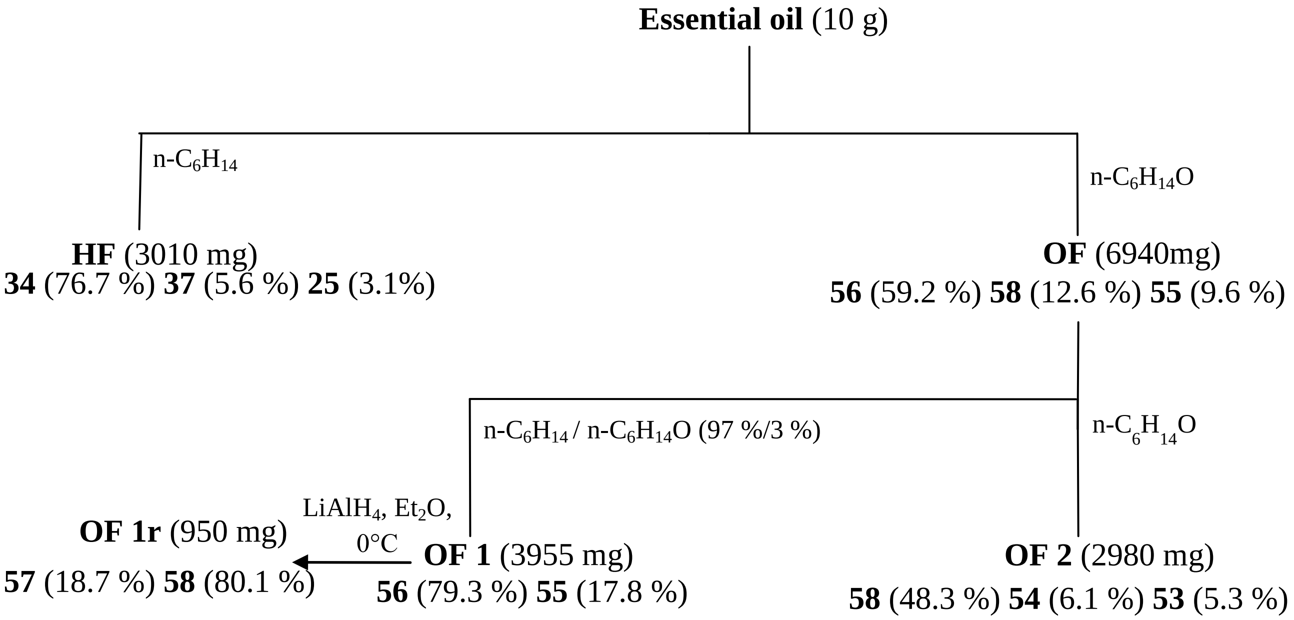

Figure 1. Fractionation of *E. maritimum* essential oil and derivative synthesis of **57** and **58**

2.4. Reduction of fraction OF 1

A part of the fraction **OF 1** (1010 mg) was dissolved in dry diethyl ether (40 mL) and carefully added to a suspension of lithium aluminium hydride (250 mg) in dry diethyl ether (60 mL) at 0°C. The mixture was stirred at room temperature and then refluxed for 3 h. The reaction mixture was hydrolyzed by the addition of 15 % sodium hydroxide solution (2 mL) and cold water. The organic layer was separated, washed with water to neutrality, dried over sodium sulphate and concentrated under vacuum. The reduction displayed a mixture (950 mg) **OF 1r** of **57** (18.7 %) and **58** (80.1 %) as main components.

2.5. GC analysis

GC analysis were carried out using a Perkin-ElmerAutosystem XL GC apparatus equipped with dual flame ionization detection (FID) system and two fused-silica capillary columns (60 m, 0.22 mm I.D., film thickness 0.25 μm), Rtx-1 (polydimethylsiloxane) and Rtx-wax (polyethyleneglycol). The oven temperature was programmed from 60 °C to 230 °C at 2 °C/min and then held isothermally at 230 °C for 35 min. Injector and detector temperature was maintained at 280 °C. Samples were injected in the split mode (1/50), using helium as carrier gas (1 mL/min); the injection volume was 0.2 μL of pure oil. Retention indices (RI) of compounds were determined relative to the retention times of series of *n*-alkanes (C5-C30) with linear interpolation, using the Van den Dool and Kratz equation [21] and software from Perkin-Elmer. Component relative concentrations were calculated based on GC peak areas without using correction factors.

2.6. GC-MS analysis

Oil samples were also analysed using a Perkin-Elmer Turbo mass detector (quadrupole), coupled to a Perkin-Elmer Autosystem XL, equipped with fused-silica capillary columns Rtx-1 and Rtx-Wax. Carrier gas: helium (1 mL/min), ion source temperature: 150 °C, oven temperature programmed from 60 °C to 230 °C at 2 °C/min and then held isothermally at 230 °C (35 min), injector temperature: 280 °C, energy ionization: 70 eV, electron ionization mass spectra were acquired over the mass range 35-350 Da, split: 1/80, injection volume: 0.2 μL of pure oil.

2.7. Identification of components

The methodology carried out for identification of individual components was based on: i) comparison of calculated retention indices (RI), on polar and apolar columns, with those of authentic compounds or literature data [22]; ii) computer matching with commercial mass spectral libraries [23] and comparison of mass spectra with those of our own library of authentic compounds or literature data [22].

2.8. Corrosion test

2.8.1. Preparation of materials

Mild steel coupons containing 0.09 wt.% (P), 0.38 wt.% (Si), 0.01 wt.% (Al), 0.05 wt.% (Mn), 0.21 wt.% (C), 0.05 wt.% (S) and the remainder iron (Fe) used for weight loss measurements. The surface preparation of the mild steel coupons (2 cm x 2 cm) was carried out with emery papers by increasing grades (400, 600 and 1200 grit size), then degreased with AR grade ethanol and dried at room temperature before use.

The aggressive solutions of 1.0 M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water. The stock solution of *E. maritimum* essential oil was prepared by dissolving at 1/10^e in ethanol as 10 mg/mL solution which was used as inhibitor. A specific volume was taken from the stock solution and added directly to 1M HCl solution to prepare the desired concentration in range from 0.25 to 2 mg/mL. All reagents used for the study were of analytical grade.

2.8.2. Weight loss measurements

Effect of concentration of inhibitors

Weight loss tests were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 mL with and without the presence of 2 mg/mL of different fractions and addition of different concentrations of *E. maritimum* oil ranging from 0.25 to 2 mg/mL. The immersion time for the weight loss was 6 h at 298 K. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Triplicate experiments were performed in each case and the mean value of the weight loss is reported using an analytical balance (precision ± 0.1 mg). Weight loss allowed us to calculate the mean corrosion rate as expressed in mg.cm^{-2} h^{-1}.

The corrosion rate (W) and inhibition efficiency E_w (%) were calculated according to the Eqs. (1) and (2) respectively:

$$W = \frac{\Delta m}{S.t} \qquad (1)$$

$$E_w\,\% = \frac{W_0 - W_{inh}}{W_0} \times 100 \qquad (2)$$

where Δm (mg) is the specimen weight before and after immersion in the tested solution, W_0 and W_{inh} are the values of corrosion weight losses (mg/cm^2.h) of mild steel in uninhibited and inhibited solutions, respectively, S is the area of the mild steel specimen (cm^2) and t is the exposure time (h).

Effect of temperature

The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition. The change of the corrosion rate with the temperature was studied in 1M HCl during 1 h of immersion, both in the absence and presence of inhibitor at a concentration corresponding to the maximum inhibition efficiency. For this purpose, gravimetric experiments were performed at different temperatures (303–343 K).

To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. (3) and transition state Eq. (4) were used [24]:

$$W = A \exp(-E_a/RT) \quad (3)$$

$$W = (RT/Nh) \exp(\Delta S°_a/R) \exp(-\Delta H°_a/RT) \quad (4)$$

where E_a is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius pre-exponential factor, h is the Plank's constant, N is the Avogrado's number, $\Delta S°_a$ is the entropy of activation and $\Delta H°_a$ is the enthalpy of activation.

2.8.3. Adsorption isotherm

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitors must be calculated with several adsorption isotherms, including Langmuir, Frumkin, and Temkin. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitor in acidic media have been evaluated from the Weight loss measurements.

3. RESULTS AND DISCUSSION

3.1. Essential oil composition

The identification of essential oil components of *E. maritimum* was carried out by using GC and GC/MS. 58 components were identified in the essential oil by comparison of their EI-MS and their retention indices (RI) with those of our own authentic compound library (Table 1).

The essential oil was dominated by oxygenated sesquiterpenes (57.9 %). 4βH-cadin-9-en-15-al **56** (36.5 %), germacrene D **34** (31.6 %), 4βH-cadin-9-en-15-ol 58 (8.3 %) and 4βH-muurol-9-en-15-al **55** (6.5 %) were the main components. *E. maritimum* essential oil (10 g) was chromatographed by an automatized flash chromatography system (Figure 1). The fractionation led one hydrocarbon fraction **HF** (3010 mg) and one oxygenated fraction **OF** (6940 mg). The polar fraction was further chromatographed leading two oxygenated sub-fractions **OF 1** and **OF 2**. All fractions were also analyzed by using GC and GC/MS. The main components of each fraction, their percentages and their number (corresponding to the order of elution on apolar column) are reported in Fig. 1. The fraction **HF** was dominated by germacrene D **34** (76.7 %) and bicyclogermacrene **37** (5.6 %). The fraction **OF** exhibited 4βH-cadin-9-en-15-al **56** (59.2 %), 4βH-cadin-9-en-15-ol **58** (12.6 %) and 4βH-muurol-9-en-15-al **55** (9.6 %) as major components. The sub-fraction **OF 1** was characterized by a high amount of uncommon sesquiterpenic aldehydes 4βH-cadin-9-en-15-al **56** (79.3 %) and 4βH-muurol-9-en-15-al **55** (17.8 %). In order to test anticorrosive power of both alcohol analogues **57** and **58**, fraction **OF 1** was reduced with $LiAlH_4$ and give a mixture called **OF 1r** with 4βH-cadin-9-en-15-ol **57** (18.7 %) and 4βH-muurol-9-en-15-ol **58** (80.1 %). Finally, the sub-fraction **OF 2** was characterized by high content of alcohol sesquiterpenic alcohols such as 4βH-cadin-9-en-15-ol **57** (48.3 %), eudesma-4,7-diene-1β-ol **54** (6.1 %) and α-cadinol **53**(5.3%) (Fig.2).

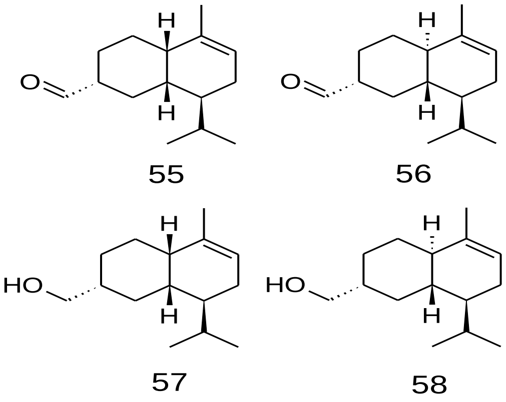

Figure 2. Structures of the main components of the oxygenated fraction (**OF**) from Corsican *E. maritimum* essential oil: 4βH-muurol-9-en-15-al **55**, 4βH-cadin-9-en-15-al **56**, 4βH-muurol-9-en-15-ol **57** and 4βH-cadin-9-en-15-ol **58**.

Table 1. Essential oil composition of *E. maritimum* and its sub-fractions.

N°^{a}	Compounds	LRI^{b}	RI$_{A}^{c}$	RI$_{P}^{d}$	EO^{e}	HF^{e}	OF^{e}	OF 1^{e}	OF 2^{e}	OF 1r^{e}
1	α-Pinene	936	930	994	0.1	0.1	-	-	-	-
2	6-Methylhept-5-ene-2-one	972	967	1570	tr	-	0.1	tr	-	-
3	2-Pentyl-furane	981	975	1201	tr	-	tr	tr	-	-
4	Octanal	981	977	1290	tr	-	tr	tr	-	-
5	Myrcene	987	983	1130	0.1	0.1	-	-	-	-
6	1,2,3-Trimethylbenzene	1011’	1006	1294	tr	0.1	-	-	-	-
7	Limonene	1025	1019	1166	tr	0.1	-	-	-	-
8	*cis*-Verbenol	1132	1126	1618	0.1	-	0.3	-	0.7	-
9	*trans*-Verbenol	1132	1130	1637	0.1	-	0.2	-	0.5	-
10	(*E*)-Non-2-enal	1139	1144	1394	0.1	-	0.1	tr	-	-
11	Methyl-4-acetophenone	1156	1153	1731	0.1	-	0.4	tr	-	-
12	Decanal	1180	1182	1498	tr	-	0.1	tr	-	-
13	2,4,6-Trimethylbenzaldehyde	1280	1281	1827	0.1	-	0.1	tr	-	-
14	2,4,5-Trimethylbenzaldehyde	1305	1297	1846	tr	-	0.4	0.1	-	-
15	2,3,6-Trimethylbenzaldehyde	1314	1318	1935	0.5	-	0.3	0.5	-	-
16	α-Cubebene	1355	1346	1452	tr	0.1	-	-	-	-
17	(*Z*)-β-Damascenone	1343	1349	1820	tr	-	tr	tr	-	-
18	α-Copaene	1371	1373	1447	0.5	1.4	-	-	-	-
19	α-Ylangene	1372	1374	1476	tr	tr	-	-	-	-
20	β-Bourbonene	1374	1375	1474	0.1	0.2	-	-	-	-
21	β-Elemene	1384	1385	1555	0.2	0.4	-	-	-	-
22	β-Patchoulene	1388	1394	1475	0.7	2.4	-	-	-	-
23	β-Gurjunene	1404	1405	1591	0.1	0.1	-	-	-	-
24	α-Gurjunene	1413	1411	1524	tr	tr	-	-	-	-
25	*cis*-α-Bergamotene	1414	1416	1480	0.8	3.1	-	-	-	-

26	β-Ylangene	1420	1420	1562	0.5	0.8	-	-	-	-
27	α-Sesquiphellandrene	1428	1430	1765	0.1	0.5	-	-	-	-
28	β-Copaene	1430	1431	1581	0.1	0.3	-	-	-	-
29	*trans*-α-Bergamotene	1434	1435	1580	0.1	0.3	-	-	-	-
30	Aromadendrene	1443	1440	1611	0.1	0.1	-	-	-	-
31	α-Humulene	1455	1449	1665	0.3	0.8	-	-	-	-
32	γ-Muurolene	1474	1468	1681	tr	0.1	-	-	-	-
33	α-Curcumene	1473	1471	1682	tr	tr	-	-	-	-
34	Germacrene D	1479	1478	1659	31.6	76.7	-	-	-	-
35	β-Sélinene	1486	1483	1712	tr	tr	-	-	-	-
36	4-*ep*-Cubebol	1490	1487	1870	0.1	-	0.2	-	0.4	-
37	Bicyclogermacrene	1494	1491	1979	1.8	5.6	-	-	-	-
38	α-Muurolene	1496	1494	1719	tr	0.1	-	-	-	-
39	β-Bisabolene	1503	1498	1720	0.1	0.3	-	-	-	-
40	γ-Cadinene	1507	1505	1720	0.2	0.4	-	-	-	-
41	Cubebol	1514	1509	1924	tr	-	0.1	-	0.3	-
42	δ-Cadinene	1520	1513	1700	0.7	2.5	-	-	-	-
43	Cadina-1,4-diene	1523	1526	1763	tr	0.1	-	-	-	-
44	(*E*)-Nerolidol	1553	1549	2037	0.5	-	0.8	-	2.9	-
45	Spathulenol	1569	1561	2119	0.5	-	0.8	-	2.5	-
46	4α-Hydroxygermacra-1,5-diene	1571	1565	2296	0.9	-	1.3	-	4.4	-
47	Caryophyllene oxide	1578	1570	1950	0.1	-	0.2	0.5	-	-
48	4β-Hydroxygermacra-1,5-diene	1580	1571	2042	0.1	-	0.2	-	0.7	-
49	Muurola-4,10-dien-8α-ol	1594	1597	2165	0.5	-	0.8	-	2.9	-
50	Aromadendrene oxide	1623	1618	2002	0.4	-	0.9	0.7	-	-
51	τ-Muurolol	1633	1634	2143	0.5	-	0.8	-	3.3	-
52	τ-Cadinol	1633	1638	2163	0.9	-	1.1	-	4.1	-
53	α-Cadinol	1643	1645	2227	1.5	-	1.8	-	5.3	-
54	Eudesma-4,7-diene-1β-ol	1671	1669	2354	0.5	-	1.5	-	6.1	-
55	4βH-Muurol-9-en-15-al	-	1684	2163	6.5	-	9.6	17.8	-	-
56	4βH-Cadin-9-en-15-al	-	1684	2173	36.5	-	59.2	79.3	-	-
57	4βH-Muurol-9-en-15-ol	-	1734	2422	0.1	-	0.4	-	0.9	18.7
58	4βH-Cadin-9-en-15-ol	-	1742	2452	8.3	-	12.6	-	48.3	80.1
	Total identified				97.1	96.7	94.3	98.9	83.3	98.8
	Hydrocarbon compounds				38.2	96.7	-	-	-	-
	Oxygenated compounds				58.9	-	94.3	98.9	83.3	98.8
	Hydrocarbon monoterpenes				0.2	0.3	-	-	-	-
	Oxygenated monoterpenes				0.2	-	0.5	-	1.2	-
	Hydrocarbon sesquiterpenes				38	96.3	-	-	-	-
	Oxygenated sesquiterpenes				57.9	-	92.3	98.3	82.1	98.8
	Other Hydrocarbon compounds				-	0.1	-	-	-	-

Other oxygenated compounds	0.8	-	1.5	0.6	-	-

[a] Order of elution is given on apolar coloumn (Rtx-1)

[b] Retention indices from literature on the apolar column Ri_a/ reported from references [12]

[c] Retention indices on the Rtx-1 apolar column

[d] Retention indices on the Rtx-wax polar column

[e] Percentages are given on the apolar column except for compounds with the same Ria (percentages are given on the polar column) ; tr : Percentages below to 0.1 ; EO : Essential oil ; HF : Hydrocarbon fraction ; OF : Oxygenated fraction ; OF 1, OF 2 and OF 1r : oxygenated sub-fractions.

3.2. Corrosion tests

3.2.1. Effect of Inhibitor Concentrations

The values of percentage inhibition efficiency Ew (%) and corrosion rate (W) obtained from weight loss method in 1M HCl without and with different concentrations of *E. maritimum* essential oil at 298 K are summarized in Table 2 and Fig. 3.

From Fig. 3, it is very clear that the *EM* oil inhibits the corrosion of mild steel in1 M HCl solution, at all concentrations used in this study, and the corrosion rate (W) decreases continuously with increasing additive concentration at 298 K. Indeed, corrosion rate values of mild steel decrease when the inhibitor concentration increases while E_w (%) values of *EM* oil increase with the increase of the concentration.

Table 2. Weight loss results of mild steel in 1M HCl without and with different concentrations of *E. maritimum* essential oil (*EM* oil) (*t*= 6h, *T*= 298 K).

EM oil concentrations (mg/mL)	W (mg/h.cm^2)	E_w (%)
0	0.381	--
0.25	0.117	69.36
0.5	0.096	74.72
1	0.062	83.66
1.5	0.037	90.18
2	0.008	97.91

Table 2 shows the inhibition efficiencies of the inhibitor at different concentrations in 1M HCl for mild steel. The results reveal that inhibition efficiency increases sharply with increase in concentration, indicating that the extent of inhibition is dependent on the amount of *EM* oil (concentration-dependent). The maximum Ew is 97.91 % at 2 mg/mL and the inhibition is estimated to be higher than 65 % even at 0.25 mg/mL and its protection is 90% at 1.5 mg/mL, which indicates that *E. maritimum* essential oil is a good inhibitor for mild steel in 1M HCl.

Under similar conditions, Ew of *Mentha spicata* oil is 97% at 2 mg/mL [6]. Therefore, comparing with some essential oils such as *Mentha pulegium* (80% at 2.76 mg/mL) [4] and *Helichrysum italicum* subsp. *italicum* (82.33 % at 2 mg/mL) [11], *E. maritimum* essential oil shows better inhibition performance. This behavior could be explained by the adsorption of the essential oil components of the *EM* oil onto the mild steel surface resulting in the blocking of the reaction sites, and protection of the mild steel surface from the attack of the corrosion active ions in the acid medium [9]. Due to the fact that *E. maritimum* essential oil is a mixture of various compounds containing mainly oxygen which can be adsorbed on the corroded metal it is hard to decide which of these components is responsible for this inhibition.

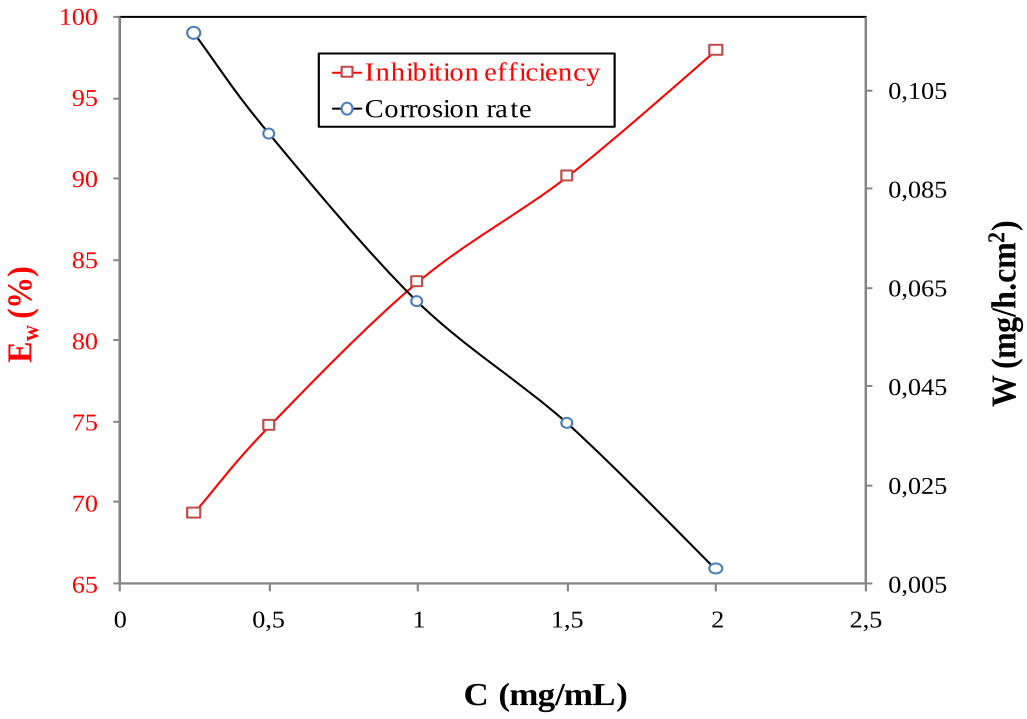

Figure 3. Variation of corrosion rate (W) and inhibition efficiency (Ew) of corrosion of mild steel in 1 M HCl with different concentration of *EM* oil.

In order to determine the components responsible for corrosion activity of the essential oil of *E. maritimum*, firstly, we have studied separately the behavior of oxygenated fraction (**OF**) and hydrocarbon fraction (**HF**) obtained by the oil CC-chromatography. We have observed that the OF seems to be responsible for the observed corrosion activity of the global essential oil. Indeed, the inhibition efficiency of this fraction was 91.29% while that of the **HF** is 67.86% at 2 mg/mL (Table 3). This result led us to seek advantage components responsible for the behavior of the **OF** against corrosion of steel in HCl 1M. Thus, we performed fractionation of **OF** in two fractions: **OF 1** (rich in compounds **55** and **56**) and **OF 2** (rich in compound **58**) (Fig. 1).

The study of behavior of these two fractions shows that **OF 1** has important efficiency (89.91% at 2 mg/mL) than the **OF 2** (83.16% at 2 mg/mL) (Table 3). In order to ensure the importance of the **OF 1** in the inhibition of corrosion, we have realized its transformation into compounds of the fraction **OF 2**, via its reduction by $LiAlH_4$ (fraction **OF 1r**) (Fig. 1). The inhibition efficiency of the latter fraction is low (74.34% at 2 mg/mL) than the fraction **OF 1** (89.91% at 2 mg/mL) (Table 3). This result shows the importance of sesquiterpenic aldehydes **55** and **56**, especially **56** (79.3%), in the inhibition of corrosion of steel in 1M HCl.

However, the sub-fraction **OF 2** was characterized, in addition to the compound **58** (48.3%), by high content of sesquiterpenic alcohols such as (*E*)-Nerolidol **44** (2.9 %), Spathulenol **45** (2.5 %), Muurola-4,10-dien-8α-ol **49** (2.9 %), τ-Muurolol **51** (3.3 %), τ-Cadinol **52** (4.1 %), α-Cadinol **53** (5.3 %) and Eudesma-4,7-diene-1β-ol **54** (6.1 %), and therefore, the importance of inhibitory effectiveness of this sub-fraction (84.13%) compared to the sub-fraction **OF 1r** may be due to the synergistic effect of different sesquiterpenic alcohols.

Table 3. Gravimetric results of mild steel in 1M HCl with addition of 2 mg/mL of *E. maritimum* essential oil and its sub-fractions (*t*= 6h, *T*= 298 K).

Compounds	EM oil	OF	OF 1	OF 2	OF 1r	HF
34 (%)	31.6	-	-		-	76.7
37 (%)	1.8	-	-		-	5.6
44 (%)	0.5	0.8	-	2.9	-	-
45 (%)	0.5	0.8	-	2.5	-	-
49 (%)	0.5	0.8	-	2.9	-	-
51 (%)	0.5	0.8	-	3.3	-	-
52 (%)	0.9	1.1	-	4.1	-	-
53 (%)	1.5	1.8	-	5.3	-	-
54 (%)	0.5	1.5	-	6.1	-	-
55 (%)	6.5	9.6	17.8	-	-	-
56 (%)	36.5	59.2	79.3	-	-	-
57 (%)	0.1	0.4	-	0.9	18.7	-
58 (%)	8.3	12.6	-	48.3	80.1	-
Efficacité E_w (%)	97.91	91.28	89.91	83.16	74.34	67.86

3.2.2. Effect of temperature and activation parameters Ea, ΔS°a, ΔH°a.

The data of corrosion rates and corresponding efficiency (Ew) collected were presented in Table 4.

Table 4. Corrosion parameters obtained from weight loss for mild steel in 1M HCl containing 2 mg/mL of *EM* oil at different temperatures.

T (K)	W_{inh} (mg/h.cm^2)	W_0 (mg/h.cm^2)	E_w (%)
303	0.237	4.178	94.33
313	0.567	7.417	92.43
323	1.5317	12.678	87.92
333	3.913	19.369	79.8
343	6.192	20.87	70.33

Examination of this Table reveals that the corrosion rate (W) increases both in the uninhibited and inhibited acid solution with the rise of temperature. The presence of inhibitor leads to decrease of the corrosion rate. Also, we note that the efficiency (Ew %) depends on the temperature and decreases with the rise of temperature from 303 to 343 K. The decrease in inhibition efficiency with increase in temperature may be attributed to can be attributed to the increased desorption of inhibitor molecules from metal surface and the increase in the solubility of the protective film or the reaction products precipitated on the surface of the metal that might otherwise inhibit the reaction. This is in accordance with our previous results [7,10].

In order to calculate activation parameters of the corrosion reaction such as activation energy E_a, activated entropy $\Delta S°_a$ and enthalpy $\Delta H°_a$, the Arrhenius equation and its alternative formulation called transition state equation were employed [24]. The activation corrosion energy (E_a) is calculated by linear regression between Ln W and 1/T (Fig. 4), and the result is shown in Table 5.

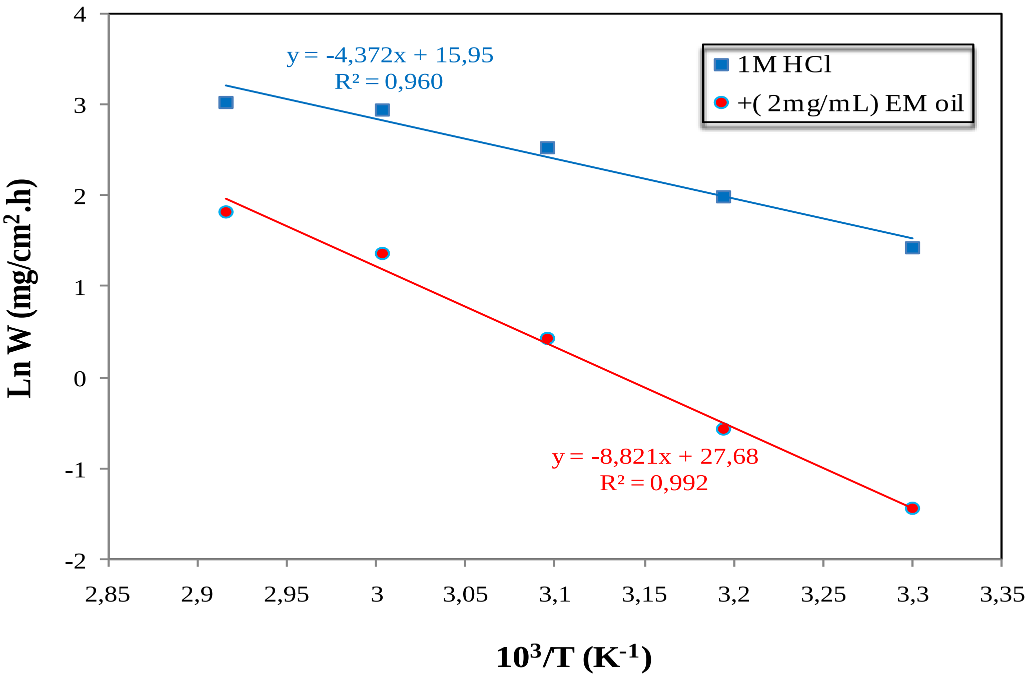

Figure 4. Arrhenius plots for mild steel corrosion rates (W) in 1M HCl in the absence and presence of 2 mg/mL of *EM* oil**.**

The logarithm of the corrosion rate of steel Ln W can be represented as straight-lines function of 10^3/T with the linear regression coefficient (R^2) was close to 1, indicating that the steel corrosion in hydrochloric acid can be elucidated using the kinetic model. The activation energy (E_a) values were calculated from the Arrhenius plots (Fig. 4) and the results are shown in Table 5.

The calculated values of activation energies from the slopes are 36.38 and 73.39 Kj/mol for free acid and with the addition of 2 mg/mL of *EM* oil, respectively. We remark that the activation energy increases in the presence of inhibitor. The higher E_a values, for inhibited solution than the uninhibited one, indicate that a strong inhibitive action of the additives by increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the mild steel surface [10]. According to Orubite et al. [25], the activation energy for physical adsorption mechanism should be less than 80kJ/mol. The higher Ea values in the presence of inhibitor compared to the blank solution indicates that the inhibitor will be effective at low temperatures, but efficiencies will be diminished at higher temperatures [11].

Fig. 5 shows a plot of Ln (W/T) against $10^3/T$. Straight lines are obtained with a slope of ($-\Delta H°_a/R$) and an intercept of ($\mathrm{Ln}(R/Nh) + (\Delta S°_a/R)$) from which the values of $\Delta H°_a$ and $\Delta S°_a$ are calculated and listed in Table 5.

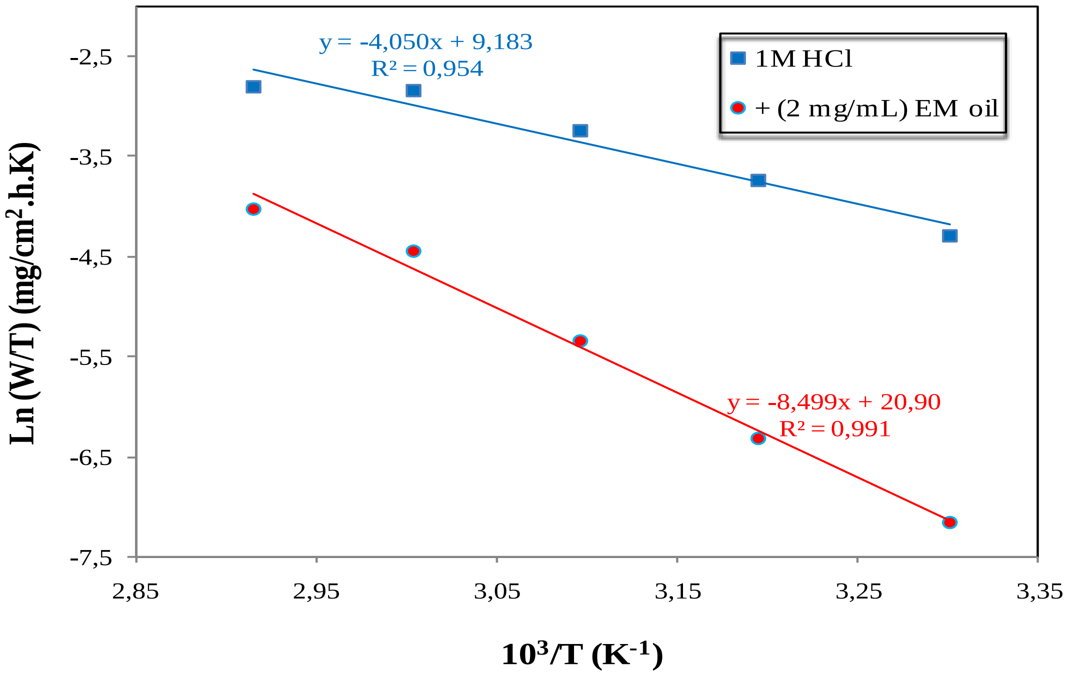

Figure 5. Transition-state plots for mild steel corrosion rates (W) in 1M HCl in absence and in presence of 2 mg/mL of *EM* oil.

Table 5. Activation parameters E_a, ΔS_a^o, $\Delta H°_a$ of the dissolution of mild steel in 1M HCl in the absence and presence of 2 mg/mL of *EM* oil.

Inhibitor	E_a (KJ. mol^{-1})	$\Delta H°_a$ (KJ.mol^{-1})	$E–\Delta H°_a$ (KJ. mol^{-1})	$\Delta S°_a$ (J. mol-1.K^{-1})
HCl 1M	36.38	33.69	2.69	-121.28
+2 mg/mL *EM* oil	73.39	70.70	2.69	-23.79

Moreover, inspection of the data of Table 5 reveals that the positive signs of $\Delta H°_a$ both in the absence and presence of 2 mg/mL of *EM* oil reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow [26]. Typically, enthalpy of physical adsorption process is lower than 80 kJ/mol while the enthalpy of chemisorption process approaches 100 kJ/mol [27]. The value of the obtained enthalpy, therefore, suggests physical adsorption of the components of the *EM* oil on the surface of the metal.

The average difference value of the E_a–$\Delta H°_a$ is 2.69 kJmol^{-1}, which is approximately equal to the average value of RT (2.69 kJ mol^{-1}) at the average temperature (323 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known Eq. (5) of perfect gas:

$$E_a - \Delta H°_a = RT \quad (5)$$

On the other hand, Large and negative values of entropies ($\Delta S°_a$) imply 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 [28].

3.3. Adsorption isotherm considerations

The adsorption process of inhibitor depends on the its electronic characteristics, the nature of metal surface, temperature, steric effects and the varying degrees of surface-site activity [29]. In fact, the solvent H_2O molecules could also be adsorbed at the metal/solution interface. Therefore, the adsorption of inhibitor molecules from the aqueous solution can be considered as a quasi-substitution process between the inhibitor in the aqueous phase $Inh_{(sol)}$ and water molecules at the electrode surface $H_2O_{(ads)}$ [30]:

$$Org_{(sol)} + xH_2O_{(ads)} \leftrightarrow xH_2O_{(sol)} + Org_{(ads)} \quad (6)$$

where x is the size ratio, that is, the number of water molecules re-placed by one organic inhibitor.

To obtain an effective adsorption of an inhibitor on metal surface, the interaction force between metal and inhibitor must be greater than the interaction force of metal and water molecule. The corrosion adsorption processes can be understood using adsorption isotherm. Langmuir adsorption isotherm is attributing to physisorption or chemisorption phenomenon while Temkin adsorption isotherm gives an explanation about the heterogeneity formed on themetal surface. Chemisorption is attributed to Temkin isotherm [31,32]. Here, Langmuir, Frumkin and Temkin adsorption isotherms were applied in order to explain the adsorption process of *EM* essential oil on the mild steel surface:

Langmuir : $C/\theta = 1/K + C$ (7)
Temkin : $\mathrm{Ln}(C/\theta) = \mathrm{Ln}K - g\theta$ (8)
Frumkin : $\mathrm{Ln}[C * (\theta/1-\theta)] = \mathrm{Ln}K + g\theta$ (9)

Where θ is the surface coverage, K is the adsorption–desorption equilibrium constant, C is the concentration of inhibitor and g is the adsorbate parameter.

The dependence of the fraction of the surface covered θ obtained by the ratio E%/100 as function of the oil concentration (C_{inh}) was graphically fitted for these various adsorption isotherms.

From Fig 6, it is concluded that Langmuir isotherm shows the best correlation with the experimental data (correlation factor equal to unity (0.993)). This result indicated that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species [33].

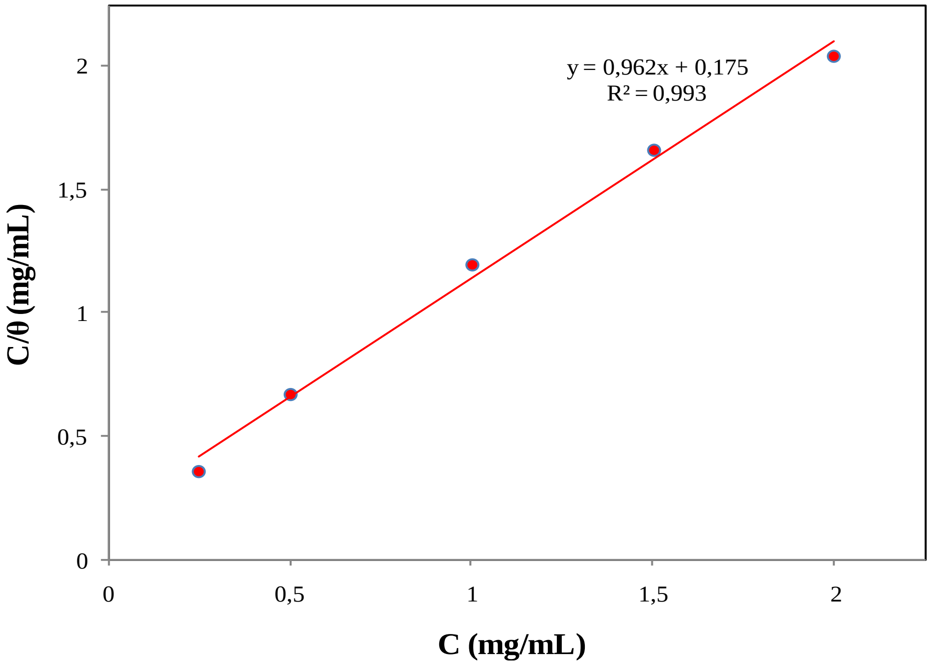

Figure 6. Langmuir adsorption isotherm of *EM* oil on the mild steel surface

The free energy of adsorption $\Delta G°_{ads}$, also can be calculated using the following equation:

$$b = \frac{1}{55,5}.\exp(-\frac{\Delta G°_{ads}}{R.T}) \qquad (10)$$

where R is the universal gas constant, T is the thermodynamic temperature, and the value of 55.5 is the concentration of water in the solution in mol/L (10^3 mg/mL).

The calculated value of free energy of adsorption was found to be $\Delta G°_{ads} = -21.45$ kJmol^{-1}, where adsorption–desorption equilibrium constant K value was obtained from the linear regression of Langmuir isotherm (K= 5.71 mL/mg). The negative value of $\Delta G°_{ads}$ indicates that the inhibitor, in this case *EM* essential oil is spontaneously adsorbed onto the mild steel surface. It is well known that values of $\Delta G°_{ads}$ around −20 kJmol^{-1} or lower are associated with the physiosorption phenomenon where the electrostatic interaction assemble between the charged molecule and the charged metal, while those around −40 kJmol^{-1} or higher are associated with the chemiosorption phenomenon where the sharing or transfer of organic molecules charge with the metal surface occurs [34]. Hence, it is clear that *EM* essential oil is physically adsorbed onto the mild steel surface. Moreover, the decrease of inhibition efficiency with the increase in temperature may supports that the adsorption of *EM* essential oil on the mild steel surface is physical in nature. As the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency.

3.4. Mechanism of inhibition

The *EM* essential oil was dominated by oxygenated compounds (> 58 %). these compounds contain Oxygen atoms in functional groups (O–H, C=O, C–O,) which meets the general characteristics of typical corrosion inhibitors. Accordingly, the inhibitive action of *EM* oil could be attributed to the adsorption of its components on the mild steel surface. Thus, it is reasonable to deduce that the oxygenated compounds in *EM* oil exhibit the inhibition performance. In aqueous acidic solution, the organic molecules of *EM* oil exist either as neutral molecules or in the form of protonated organic molecules (cation). Generally, two modes of adsorption are considered on the metal surface in acid media. In one mode, the neutral molecules may be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the oxygen atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor–acceptor interactions between their π-electrons and vacant d-orbitals of surface iron. In second mode, since it is well known that it is difficult for the protonated molecules to approach the positively charged mild steel surface (H_3O^+/metal interface) due to the electrostatic repulsion. Since Cl^- have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favour more adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed Cl^- ions and protonated inhibitors [35,36].

4. CONCLUSION

The study of chemical composition and effect of *EM* essential oil and its sub-fractions on the corrosion of mild steel in 1 M HCl conducted by weight loss measurements may draw the following conclusions:

- Chemical analysis shows that 4βH-cadin-9-en-15-al **56** (36.5 %), germacrene D **34** (31.6 %), 4βH-cadin-9-en-15-ol **58** (8.3 %) and 4βH-muurol-9-en-15-al **55** (6.5 %) were the main components of *EM* essential oil;
- *EM* essential oil acts as good inhibitor for the corrosion of mild steel in 1 M HCl with inhibition efficiency 97.91 % at 2 mg/mL;
- Inhibition efficiency increases with the concentration of inhibitor and decreases with temperature;
- Inhibition efficiency on mild steel may occur by synergistic action of terpenes presents in *EM* essential oil.
- Inhibition efficiency of *EM* essential oil might be due principally to oxygenated terpenic compounds and more precisely to sesquiterpenic aldehydes 4βH-muurol-9-en-15-al **55** and 4βH-cadin-9-en-15-al **56**.

References

1. S. Kharchouf, L. Majidi, M. Bouklah, B. Hammouti, A. Bouyanzer, A. Aouniti. *Arab. J. Chem.* (2011). doi:10.1016/j.arabjc.2010.12.002.
2. L. Majidi, Z. Faska, M. Znini, S. Kharchouf, A. Bouyanzer, B. Hammouti. J. *Mater. Environ. Sci*. 1 (2010) 219.
3. S. Kharchouf, L. Majidi, M. Znini, J. Costa, B. Hammouti, J. Paolini. *Int. J. Electrochem. Sci*., 7 (2012) 10325.
4. A. Bouyanzer, B. Hammouti, L. Majidi, *Mat. Lett*. 60 (2006) 2840.
5. M. Znini, L. Majidi, A. Bouyanzer, J. Paolini, J.M. Desjobert, J. Costa, B. Hammouti, *Arab. J. Chem*. 5 (2012): 467.
6. M. Znini, M. Bouklah, L. Majidi, S. Kharchouf, A. Aouniti, A. Bouyanzer, B. Hammouti, J. Costa, S.S. Al-Deyab, *Int. J. Electrochem. Sci*. 6 (2011) 691.
7. M. Znini, L. Majidi, A. Laghchimi, J. Paolini, B. Hammouti, J. Costa, A. Bouyanzer, S. S. Al-Deyab, *Int. J. Electrochem. Sci*. 6 (2011) 5940.
8. M. Znini, J. Paolini, L. Majidi, J.-M. Desjobert, J. Costa, N. Lahhit, A. Bouyanzer, *Res. Chem. Intermed*. 38 (2012) 669.
9. G. Cristofari, M. Znini, L. Majidi, A. Bouyanzer, S.S. Al-Deyab, J. Paolini, B. Hammouti, J. Costa, *Int. J. Electrochem. Sci*. 6 (2011) 6699.
10. M. Znini, G. Cristofari, L. Majidi, A. Ansari, A. Bouyanzer, J. Paolini, J Costa, B. Hammouti, *Int. J. Electrochem. Sci*., 7 (2012) 3959.
11. G. Cristofari, M. Znini, L. Majidi, J. Costa, B. Hammouti, J. Paolini, *Int. J. Electrochem. Sci*., 7 (2012) 9024.
12. H. Coste, *Flore descriptive et illustrée de la France, de la Corse et des contrées limitrophes II.* Librairie scientifique et technique Albert Blanchart, Paris, (1980) 627.
13. C.P.P. Rama, R.C. Sudhakar, S.H. Raza, C.B.S. Dutt, *Fitoterapia*. 79 (2008) 458.
14. E. Küpeli, M. Kartal, S. Aslan, E. Yesilada, *J. Ethnopharmacol.* 107 (2006) 32.
15. Z. Yaniv, A. Dafni, J. Friedman, D. Palevitch, *J. Ethnopharmacol.* 19 (1987) 145.
16. M. H. Duffaud, *Revue Forestiere Francaise*. 50 (1998) 328.
17. M.D. Lillis, L. Costanzo, P.M. Bianco, A. Tinelli, *J. Coast. Conservat.* 10 (2004) 93.
18. R. Lisciani, E. Fattorusso, V. Surano, S. Cozzolino, M. Giannattasio, L. Sorrentino, *J. Ethnopharmacol.* 12 (1984) 263.
19. F. Darriet, M. Bendahou, J.M. Desjobert, J. Costa, A. Muselli, *Planta med.* 78 (2012) 386.
20. Conseil de l'Europe, *Pharmacopée Européenne*, Maisonneuve S. A. : Sainte Ruffine, 1996.
21. H. Dool, P. Kratz, *J. Chromatogr*. 11 (1963) 463.
22. D. Joulain, König, W.A., The atlas of spectral data of sesquiterpene hydrocarbons. EbVerlag Hamburg. (1998).
23. D. Hochmuth, D. Joulain, König, W.A., Terpenoids and related constituents of essential oils, Library of Massfinder 2.1, University of Hamburg Institute of organic chemistry Hamburg Germany. (2001).
24. F. Bentiss, M. Lebrini, M. Lagrenée, *Corros. Sci*. 47 (2005) 2915
25. K.O. Orubite, N.C. Oforka, *Mater. Lett*. 58 (2004) 1772.
26. N.M. Guan, L. Xueming, L. Fei, *Mater. Chem. Phys*. 86 (2004) 59.
27. S. Martinez, I. Stern, *Appl. Surf. Sci*. 199 (2002) 83.
28. S. Samkarapapaavinasam, M.F. Ahmed, *J. Appl. Electrochem*. 22 (1992) 390.
29. A.A. El-Awady, B.A. Abd-El-Nabey, S.G. Aziz, J. *Electrochem. Soc*. 139 (1992) 2149.
30. I. El Ouali, B. Hammouti, A. Aouniti, Y. Ramli, M. Azougagh, E.M. Essassi, M. Bouachrine, *J. Mater. Environ.* Sci. 1 (2010) 1.
31. S.P. Fakrudeen, B. Raju, *J. Mater. Environ. Sci.* 4 (2013) 326.

32. D.Wahyuningrum, S. Achmad, Y.M. Syah, B. Buchari, B. Bundjali, Ariwahjoedi, *Int. J. Electrochem. Sci*. 3 (2008) 164.
33. S. Cheng, S. Chen, T. Liu, X. Chang, Y. Yin, *Mater. Lett*. 61 (2007) 3279.
34. E. Khamis, F. Bellucci, R.M. Latanision, E.S.H. El-r, *Corrosion* 47 (1991) 677.
35. G.N. Mu, T.P. Zhao, M. Liu, T. Gu, *Corrosion*. 52 (1996) 853.
36. I. Ahamad, S. Khan, K.R. Ansari, M.A. Quraishi, *J. Chem. Pharm. Res*. 3 (2011) 703.