

# Use of *Rosmarinus officinalis* as Green Corrosion Inhibitor for Carbon Steel in Acid Medium

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## ABSTRACT

The use of *Rosmarinus officinalis* as a corrosion inhibitor for 1018 carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> has been evaluated by using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy techniques at 25°. Inhibitor concentrations were included within the range between 0 and 1000 ppm C using three extract solvents, namely acetone, hexane and methanol. Results have shown that *Rosmarinus officinalis* is a good corrosion inhibitor with its efficiency increasing with the concentration. The best efficiency was obtained with the hexanic extract. The passivating film properties of the steel were improved by the presence of flavonoids in the extract.

## KEYWORDS

Metals; Corrosion; Fourier Transform Infrared Spectroscopy; Electrochemical Techniques

## 1. Introduction

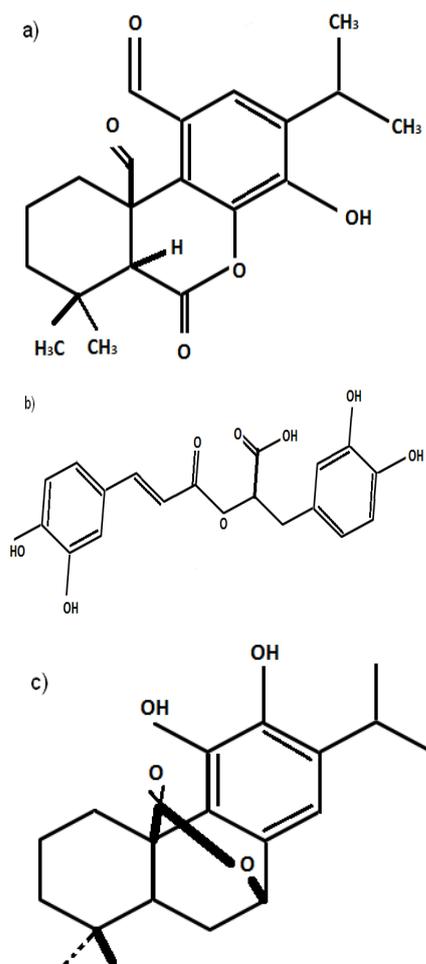
Corrosion of materials causes big losses in the economy of many countries due to the huge amount of funds needed in order to reduce it. Corrosion inhibition of metals, especially of steel, has received a lot of attention because of its widespread use in the industry such as the oil and gas, beverage, metallurgy among others, and thus, a lot of research in the field of corrosion inhibition of steel is necessary. The studies of plant extract as low-cost and eco-friendly corrosion inhibitors are of great interest from an environmental perspective and are attracting a significant level of attention [1-3]. Green inhibitors receive attention for the replacement of synthesized inorganic inhibitors which are often toxic, expensive and environmentally unfriendly [4] and have a promising future for the quality of the environment because they do not contain heavy metals or other toxic compounds. Extracts from leaves, seeds, fruits and roots contain compounds with nitrogen, sulfur and oxygen described as efficient corrosion inhibitors indifferent to the aggressive

environments [5,6]. Some examples of natural products used as corrosion inhibitors include *Parthenium hysterophorus* [7], *Capsicum annum* [8], *Lawsonia* [9], *Opuntia* [10], *Swertia aungustifolia* [11], *Ficus religeosa* [12], *heena* [13], *Datura stramonium* [14], *calotropis* [15], *Prosopis cineraria* [16], *Occimum viridis*, *Telferia occidentalis*, *Azadirachta indica* and *Hibiscus sabdariffa* [17], *Pachylobus edulis* [18] and *Dacroydes edulia* [19]. These studies have shown that organic compounds containing N, S and O have high corrosion inhibitors. Most of these organic inhibitors are adsorbed on the metal surface [20]. These green corrosion inhibitors contain, for instance, tannins, saponins, proteins, flavonoids among others.

Among the plants with known antioxidant properties, rosemary, *Rosmarinus officinalis*, an aromatic plant of Mediterranean origin is the one that has been mostly used and commercialized [21,22]. In *Rosmarinus officinalis*, the presence of at least six phenolic diterpenoids with antioxidant activity such as carnosol, carnosic acid, rosmarinic acid, rosmadial, rosmanol, epirosmanol and me-

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thyl carnosate has been reported [23-27]. The chemical structure of some of these compounds is shown in **Figure 1**. Some rosemary extracts have been used in medicine as anti-inflammatory [28] and antimicrobial agents [29]. Kliskic *et al.* [30] evaluated the first neutral phenol sub-fraction of the aqueous extract of *Rosmarinus officinalis* leaves as the corrosion inhibitor for the Al-2.5 Mg alloy in 3% NaCl at 25°C and different concentrations ranging from  $10^{-7}$  to  $10^{-3}$  M, finding that this extract acts as a cathodic type of inhibitor. On the other hand, Ouarichi *et al.* [31] used *Rosmarinus officinalis* essential oil obtained by hydro-distillation as the corrosion inhibitor for C38 steel in 0.5M  $H_2SO_4$  using weight loss measurements and polarization curves. Their results indicate that the corrosion rate is reduced and its inhibition efficiency increases with oil concentration reaching the highest value, 61%, at 1 g/L, acting as a cathodic type of inhibitor. In this work, *Rosmarinus officinalis* extracts by using different types of solvents are used as corrosion inhibitors for 1018 carbon steels in 0.5 M  $H_2SO_4$ .



**Figure 1.** Chemical structure for the main components of *Rosmarinus officinalis* showing in a) Carnosic acid, b) Rosmarinic acid and c) Carnosol.

## 2. Experimental Procedure

Corrosion tests were performed on coupons prepared from 1018 carbon steel rods containing 0.14% C, 0.90% Mn, 0.30% S, 0.030% P and as balance Fe, encapsulated in commercial epoxic resin with an exposed area of 1.0  $cm^2$ . The aggressive solution, 0.5 M  $H_2SO_4$  was prepared by dilution of analytical grade  $H_2SO_4$  with double distilled water. Dried *Rosmarinus officinalis* leaves were soaked in either methanol, acetone or hexane during 24 h and used as a stock solution and used then for preparation of the desired concentrations by dilution, without any other treatment. The resulting extract was used as a stock solution and characterized by FTIR. Weight loss experiments were carried out with carbon steel rods 2.5 cm length and 0.6 cm diameter abraded with fine emery paper until 1200 grade, rinsed with acetone, and exposed to the aggressive solution during 72 h. After a total time of exposition of 72 hours, specimens were taken out, washed with distilled water, degreased with acetone, dried and weighed accurately. Tests were performed by triplicate at room temperature (25°C). Corrosion rates, in terms of weight loss measurements,  $\Delta W$ , were calculated as follows:

$$\Delta W = (m_1 - m_2) / A \quad (1)$$

where  $m_1$  is the mass of the specimen before corrosion,  $m_2$  the mass of the specimen after corrosion, and  $A$  the exposed area of the specimen. For the weight loss tests, inhibitor efficiency,  $IE$ , was calculated as follows:

$$IE (\%) = 100(\Delta W_1 - \Delta W_2) / \Delta W_1 \quad (2)$$

where  $\Delta W_1$  is the weight loss without inhibitor, and  $\Delta W_2$  the weight loss with inhibitor. Specimens were weighed in an analytical balance with a precision of 0.1 mg. Employed electrochemical techniques included potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements, EIS. In all experiments, the carbon steel electrode was encapsulated in commercial epoxic resin, was allowed to reach a stable open circuit potential value,  $E_{corr}$ . Polarization curves were recorded at a constant sweep rate of 1 mV/s at the interval from -1000 to +1500 mV respect to the  $E_{corr}$  value. Measurements were obtained by using a conventional three electrodes glass cell with two graphite electrodes symmetrically distributed and a saturated calomel electrode (SCE) as reference with a Lugging capillary bridge. Corrosion current density values,  $I_{corr}$ , were obtained by using Tafel extrapolation by taking an extrapolation interval of 250 mV around the  $E_{corr}$  value. Inhibitor efficiency,  $IE$ , were calculated according to the following equation:

$$IE (\%) = 100(I_{corr,b} - I_{corr,i}) / I_{corr,b} \quad (3)$$

were  $I_{corr,i}$  and  $I_{corr,b}$  are the corrosion current density values with and without inhibitor respectively. Electrochemical impedance spectroscopy (EIS) tests were carried out at  $E_{corr}$  by using a signal with amplitude of 10 mV in a frequency interval of 100 mHz-100 KHz. An ACM potentiostat controlled by a desk top computer was used for the polarization curves, whereas for the EIS measurements, a model PC4 300 Gamry potentiostat was used.

### 3. Results and Discussion

#### 3.1. Gravimetric Measurements

The effect of the different extracts concentration in the weight loss for carbon steel in 0.5 M  $H_2SO_4$  is shown in **Figure 2**, where it can be seen that, regardless of the medium used for its extraction, the corrosion rate decreases with increasing the inhibitor concentration, being the most efficient one the inhibitor extracted with hexane, as can be seen in **Figure 3**, where the inhibitor efficiency values for the different extracts are plotted. The highest inhibitor efficiency was reached when 1000 ppm of inhibitor is added, around 60% for the hexanic extract, and 45% for both the acetonic and methanolic extracts. The successful inhibitory action of *Rosmarinus officinalis* could be explained by the presence of organic compounds such as carnosol, carnosic acid, rosmadial, rosmanol, epirosmanol, and methyl carnosate [23-27]. Organic compounds that contain O, S, or N or their combination have been reported as corrosion inhibitor for metals in acidic or alkaline solutions [1-7]. The adsorption of these compounds on the metal surface reduces the available area for the attack of aggressive ions such as  $SO_4^{2-}$  or  $Cl^-$ . As seen from **Figure 2**, the weight loss decreases with increasing the extract concentration due to a higher degree of surface coverage as a result of enhanced inhibitor adsorption. In order to evaluate the adsorption process of *Rosmarinus officinalis* on the 1018 carbon steel surface, Langmuir, Temkin and Frumkin adsorption isotherms were obtained according to the following equations:

$$\text{Langmuir : } \theta/1-\theta = KC_{inh} \quad (4)$$

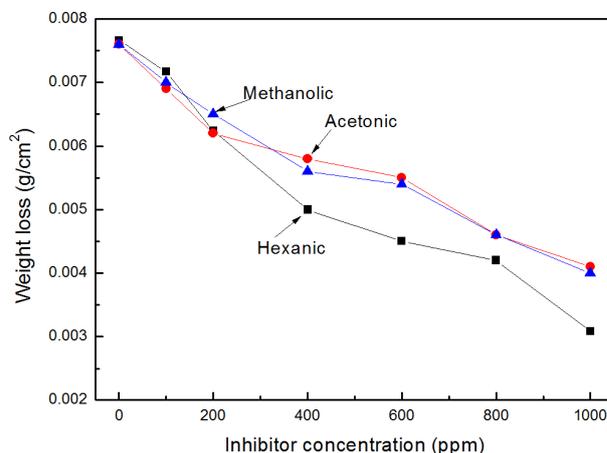
$$\text{Temkin : } \log \theta/C_{inh} = \log K - g\theta \quad (5)$$

$$\text{Frumkin : } \log \theta C_{inh}/(1-\theta) = \log K + g\theta \quad (6)$$

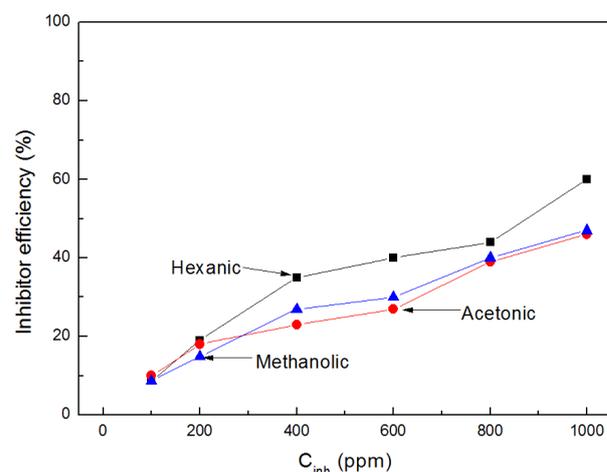
where  $\theta$  is the surface coverage,  $K$  the adsorption-desorption equilibrium constant,  $C_{inh}$  the inhibitor concentration and  $g$  the adsorbate interaction parameter. The surface coverage,  $\theta$ , was calculated as

$$\theta = (\Delta W_1 - \Delta W_2)/\Delta W_1 \quad (7)$$

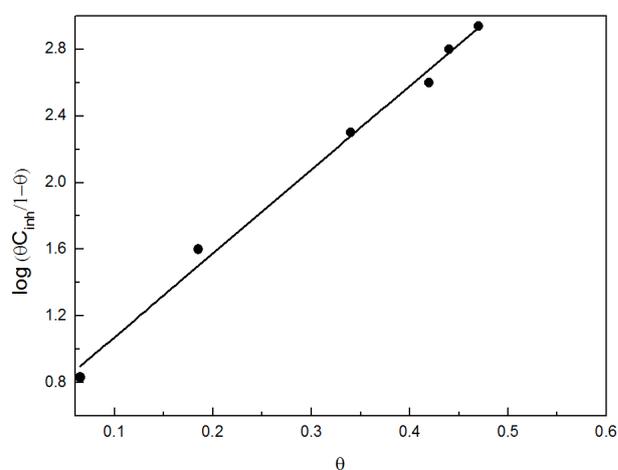
The isotherm that best fitted with the data obtained, as can be seen in the **Figure 4** was that for the Frumkin one



**Figure 2.** Weight loss as a function of *Rosmarinus officinalis* concentration for carbon steel after 72 h of exposure to 0.5 M  $H_2SO_4$  25°C using different solvents.



**Figure 3.** Inhibitor efficiency as a function of *Rosmarinus officinalis* concentration for carbon steel after 72 h of exposure to 0.5 M  $H_2SO_4$  at 25°C using different solvents.

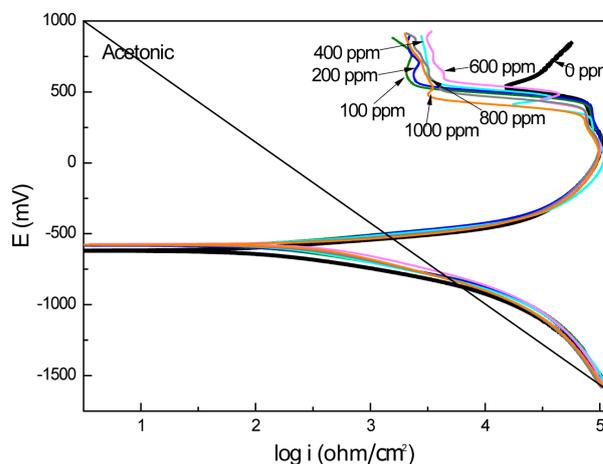


**Figure 4.** Frumkin isotherm for the adsorption of the hexanic extract of *Rosmarinus officinalis* on the surface of carbon steel in 0.5 M  $H_2SO_4$  using the weight loss data.

with an  $R^2$  value of 0.996, indicating that *Rosmarinus officinalis* adsorbed onto the carbon steel surface. From the Frumkin isotherm, the adsorption-desorption equilibrium constant  $K$  was determined as  $-0.57 \text{ L}\cdot\text{mg}^{-1}$  leading to an adsorption free-energy value of  $-37.4 \text{ kJ}\cdot\text{mol}^{-1}$ . Generally, values of the adsorption free-energy much less than  $-40 \text{ kJ}\cdot\text{mol}^{-1}$  have typically been correlated with the electrostatic interactions between organic molecules and charged metal surface (physisorption) whilst those values in the order of  $-40 \text{ kJ}\cdot\text{mol}^{-1}$  are associated with charge sharing or transfer from the organic molecules to the metal surface (chemisorption) to form a coordinate type of bond [32]. The negative value of the free-energy of adsorption value means that the adsorption process is spontaneous, while the value around  $-40 \text{ kJ}\cdot\text{mol}^{-1}$  indicates that *Rosmarinus officinalis* was chemically adsorbed on the steel surface.

### 3.2. Potentiodynamic Polarization Curves

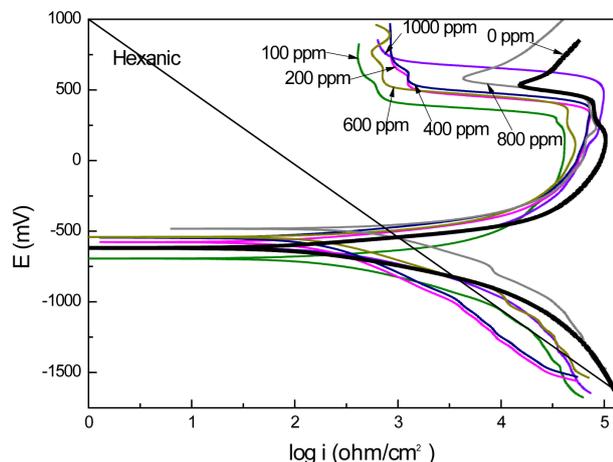
The effect of the acetic extract concentration in the polarization curves for carbon steel in  $0.5 \text{ M H}_2\text{SO}_4$  is shown in Figure 5. This figure shows an active-passive behavior in both uninhibited and inhibited solution, and it can be clearly seen that neither the  $E_{corr}$  nor the  $I_{corr}$  values were substantially affected by the inhibitor; in addition to this, neither the cathodic nor the anodic current density values were affected by the presence of the inhibitor; however, the passivation current density and the pitting potential values,  $I_{pass}$  and  $E_{pit}$  respectively were markedly affected. The fact that the anodic current density values and the anodic Tafel slopes were almost the same with or without inhibitor could be related to an absence in a change in the anodic reaction mechanism. For the uninhibited solution, the steel passive zone was very narrow, only a few millivolts wide, with an  $E_{pit}$  value close to  $544 \text{ mV}$  and an  $I_{pass}$  value was around  $12,590 \text{ A/cm}^2$ , but with inhibitor the  $E_{pit}$  value increased and the  $I_{pass}$  value decreased for almost two orders of magnitude lower. With increasing the inhibitor concentration the  $I_{pass}$  value increased, but in all cases it was lower than that value obtained for the uninhibited solution for almost one order of magnitude, and the  $E_{pit}$  value remained higher than that for the blank solution. Thus, the presence of the inhibitor clearly reacts with the environment and the steel to form adherent, compact, insoluble protective corrosion products improving the steel passive film properties formed in the uninhibited solution. If we take the  $I_{corr}$  value as a reference parameter, all the inhibitor efficiency values become negatives, indicating an increase in the  $I_{corr}$  value with the addition of the inhibitor. However, if we use the  $I_{pas}$  value as a reference parameter, we obtain the lowest inhibitor efficiency value when  $600 \text{ ppm}$  of inhibitor are added, and  $84\%$  with both  $800$  and  $1000 \text{ ppm}$ . Additionally, the cathodic Tafel slopes are



**Figure 5.** Effect of the acetic extract concentration of *Rosmarinus officinalis* in the polarization curves for carbon steel in  $0.5 \text{ M H}_2\text{SO}_4$ .

markedly more affected than the anodic one by the addition of the inhibitor, thus, it could be said that although *Rosmarinus officinalis* acts as a mixed type of inhibitor it behaves more cathodically than anodically. This indicates that *Rosmarinus officinalis* inhibits more the hydrogen evolution than the carbon steel dissolution reaction.

When the hexanic extract was used, Figure 6, polarization curves still displayed an active-passive behavior, the  $E_{corr}$  value was affected this time shifting most of the times towards nobler values except with the addition of  $100 \text{ ppm}$  which could be related to the adsorption of the organic compound at the active sites of the electrode surface, retarding the corrosion reaction [33]. The  $I_{corr}$  value did not decrease with an increase in the inhibitor concentration up to  $200 \text{ ppm}$ , but with a further increase in the inhibitor concentration the corrosion rate decreased, indicating a change in the anodic reaction mechanism (iron dissolution), corroborated by a decrease in the anodic Tafel slope with increasing concentration of *Rosmarinus officinalis*. This lowering of the anodic Tafel slope has been interpreted by some authors [33,34] as being due to 1) the adsorption of *Rosmarinus officinalis* at lower concentrations (energy effect), 2) a change in the mechanism reaction, and 3) the desorption of *Rosmarinus officinalis* at higher concentrations. In all cases, except with the addition of  $400$  or  $600 \text{ ppm}$  of inhibitor, the anodic current density values were decreased when the inhibitor was added; additionally, the cathodic current density values were decreased at all cases except when  $800 \text{ ppm}$  of inhibitor were added and the cathodic Tafel slope increased more markedly than the anodic one, indicating that the hydrogen evolution reaction is diminished exclusively by the surface blocking effect of *Rosmarinus officinalis*. The  $E_{pit}$  value increased and the  $I_{pas}$  decreased, improving, thus, the passive film proper-



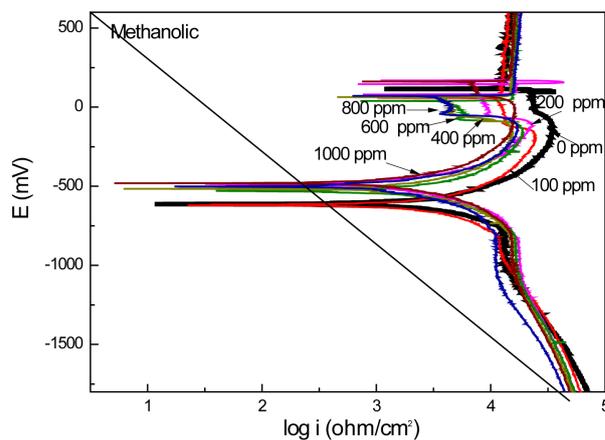
**Figure 6.** Effect of the hexanic extract concentration of *Rosmarinus officinalis* in the polarization curves for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

ties, and thus, if we use this parameter as reference, the inhibitor efficiency reached high values between 81 and 96%.

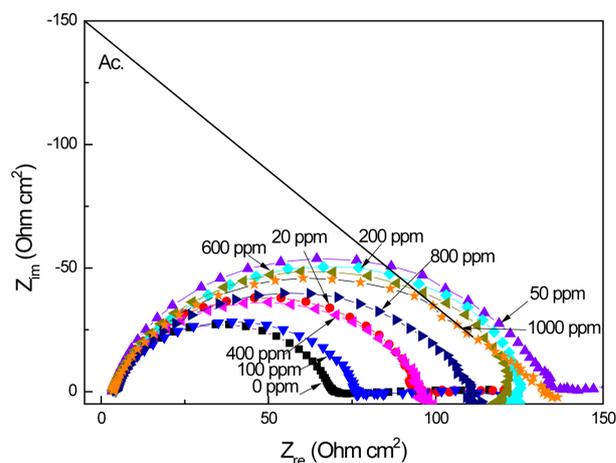
Finally, when the methanolic extract was used, the polarization curves showed an active-passive behavior, **Figure 7**, shifting the  $E_{corr}$  value towards less negative values and the  $I_{corr}$  value decreased as the inhibitor concentration increases. The passivation current density value slightly decreased but this time it was not affected as it was either with the acetonic or hexanic extracts, decreasing its value more than two orders of magnitude. At low cathodic overpotentials, a limiting current density value can be observed, which could be due to the oxygen reduction reaction, and at higher cathodic overpotentials the increase in the cathodic current density is due to the hydrogen evolution reaction. Inhibitor efficiency values calculating  $I_{corr}$  increased with increasing the inhibitor concentration, but if we use the  $I_{pas}$  values, very low or even negative values are obtained this time, indicating that little effect in the passive film properties as compared as the effect done by the acetonic or hexanic extracts. Both the cathodic and anodic Tafel slopes were affected in this case, indicating that now the inhibitor is acting as a mixed type of inhibitor, indicating that inhibitor affects both the hydrogen evolution and the anodic dissolution reaction.

### 3.3. Impedance Measurements

The effect of the acetonic extract of *Rosmarinus officinalis* concentration in the Nyquist diagrams for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> is shown in **Figure 8**. For the blank, uninhibited solution, EIS data describe at all frequencies a single depressed, capacitive loop, with its center at the real axis, indicative of a corrosion process controlled from the metal to the electrolyte through the double elec-



**Figure 7.** Effect of the hexanic extract concentration of *Rosmarinus officinalis* in the polarization curves for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Figure 8.** Effect of the acetonic extract concentration of *Rosmarinus officinalis* in the Nyquist diagrams for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

trochemical layer. The capacitive time constant at high frequencies is attributed to the reactions involved in the formation of the oxide layer [35,36] or to the oxide layer itself [37,38]. As soon as the *Rosmarinus officinalis* is added to solution, the Nyquist diagrams increase in diameter with the inhibitor concentration, indicating a more protective film formation, which probably reflects physical blocking of the steel surface due to the adsorption of the inhibitor, reaching the highest diameter with 1000 ppm. The capacitive properties of systems considered in presence of *Rosmarinus officinalis* are attributable to the dielectric properties of the surface (metal-oxide-inhibitor) adsorption layer. The loop or semicircle diameter corresponds to the double layer or charge transfer resistance,  $R_{ct}$ , equivalent to the polarization resistance,  $R_p$ , and thus, inversely proportional to the corrosion current density value,  $I_{corr}$ . Thus, we can see from **Figure 8** that the highest  $R_{ct}$  value was around 134 ohm

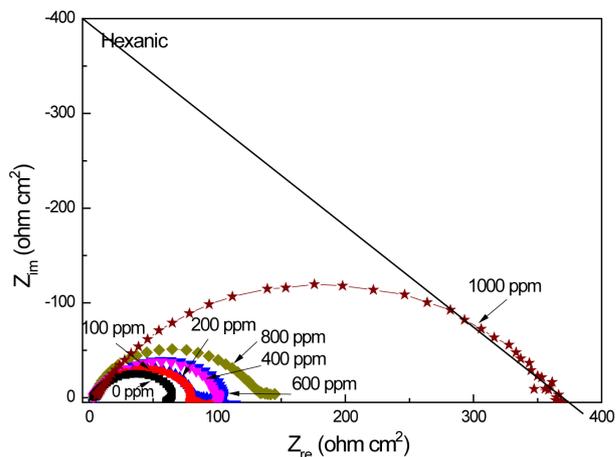
$\text{cm}^2$  obtained with the addition of 1000 ppm, whereas the lowest value, that for the uninhibited solution, was  $68 \text{ ohm cm}^2$ . This increase in the  $R_{ct}$  value is due to the adsorption of *Rosmarinus officinalis* and, after reacting with the steel and/or the environment form adherent, passive corrosion products.

When the hexanic extract of *Rosmarinus officinalis* is used, **Figure 9**, Nyquist data describe a single depressed, capacitive semicircle, with its center at the real axis, indicating that the corrosion process is controlled by the charge transfer from the steel to the electrolyte through the double electrochemical layer. As soon as the inhibitor is added, the semicircle diameter increases and this time, the biggest semicircle diameter was obtained with the addition of 1000 ppm, with a value was close to  $360 \text{ ohm cm}^2$ , almost 5 times bigger than that obtained for both the uninhibited, blank solution ( $68 \text{ ohm cm}^2$ ) or with the acetonic extract. This is due to the adsorption of the *Rosmarinus officinalis* on the steel surface, which, according to polarization curves shown in **Figure 6** form an adherent, protective passive film which protects the steel from the acidic environment. Finally, when the methanolic extract of *Rosmarinus officinalis* is used, **Figure 10**, Nyquist data describe, again, a single depressed, capacitive-like semicircle at all frequencies, with their centers in the real axis, and with their diameter increasing with the inhibitor concentration, reaching its highest value when 1000 ppm of inhibitor are added, but this time the  $R_{ct}$  value was only  $160 \text{ ohm cm}^2$ , higher than that obtained with the acetonic extract, but lower than that obtained with the hexanic extract. Inhibition efficiencies [IE(%)] can be determined according to the following equation:

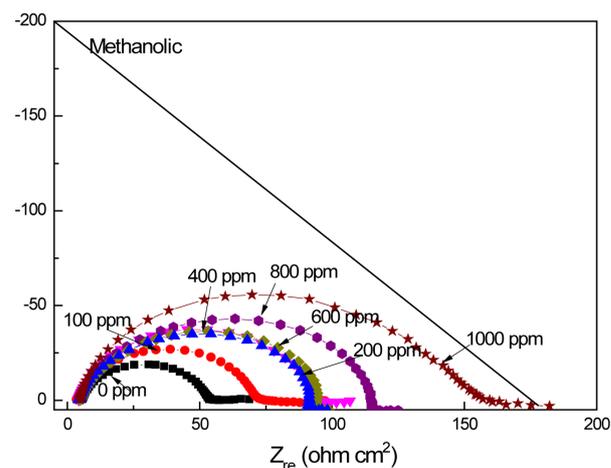
$$IE(\%) = 100(R_{ct,i} - R_{ct,b})/R_{ct,i} \quad (8)$$

where  $R_{ct,b}$  is the charge transfer resistance without inhibitor and  $R_{ct,i}$  is the charge transfer resistance with inhibitor. In the three cases it increases with the inhibitor concentration, obtaining the highest inhibitor efficiency with the addition of 1000 ppm, 81%, with the use of the hexanic extract. These results are in agreement with those obtained by El Ouarichi *et al.* [31] who used *Rosmarinus officinalis* essential oil obtained by hydrodistillation as corrosion inhibitor for C38 steel in  $0.5 \text{ M H}_2\text{SO}_4$  and found that it was a good corrosion inhibitor, with its efficiency increasing with the oil contents, reaching the highest efficiency, 61%, with a concentration of 1000 ppm. They also found that the *Rosmarinus officinalis* essential oil acted as a cathodic type of inhibitor [31].

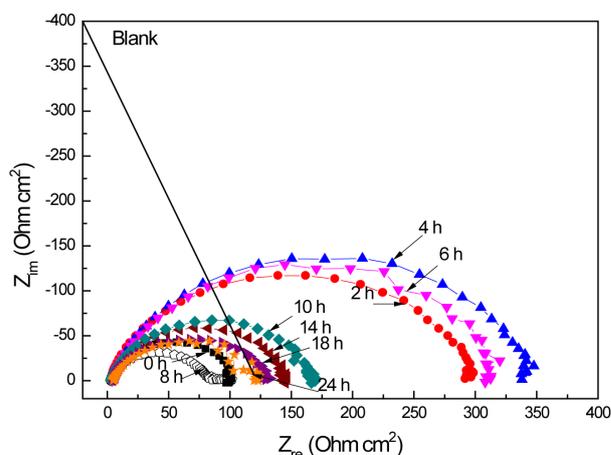
In order to see the inhibitor film stability, some long term EIS tests were performed during 24 hours and **Figure 11** shows the results for the blank, uninhibited solution. It can be seen that Nyquist semicircle diameter increases with time and reaches its highest value,  $350$



**Figure 9.** Effect of the hexanic extract concentration of *Rosmarinus officinalis* in the Nyquist diagrams for carbon steel in  $0.5 \text{ M H}_2\text{SO}_4$ .



**Figure 10.** Effect of the methanolic extract concentration of *Rosmarinus officinalis* in the Nyquist diagrams for carbon steel in  $0.5 \text{ M H}_2\text{SO}_4$ .



**Figure 11.** Variation of the Nyquist diagrams with time for carbon steel after 24 h of exposure to  $0.5 \text{ M H}_2\text{SO}_4$  in absence of *Rosmarinus officinalis*.

ohm  $\text{cm}^2$ , almost 4 times bigger than at the beginning of the test, after 4 hours of testing, and, after that time, the semicircle diameter decreases, thus, indicating that the lowest corrosion rate is reached after 4 hours of testing. For the hexanic extract, **Figure 12**, it can be seen that the semicircle diameter increases from a value close to 200 ohm  $\text{cm}^2$  at the beginning of the test, up to 70,000 ohm  $\text{cm}^2$  after 2 hours of testing, but it decreases as time increases, remaining close to 1000 ohm  $\text{cm}^2$  throughout the experiment. The results for all the extracts are summarized in **Figure 13**, where it can be seen that the  $R_{ct}$  value for both the acetic and methanolic extracts decrease after about 6 hours or so reaching the same values obtained for the uninhibited solution, and that for the hexanic extract remains at least one order of magnitude higher than that obtained with the uninhibited solution throughout the testing time, producing, thus, a very stable protective film.

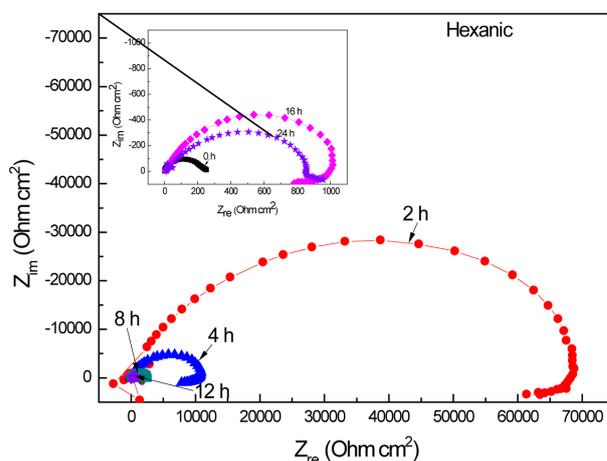
The double-layer capacitance ( $C_{dl}$ ) was calculated from the equation below:

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \quad (9)$$

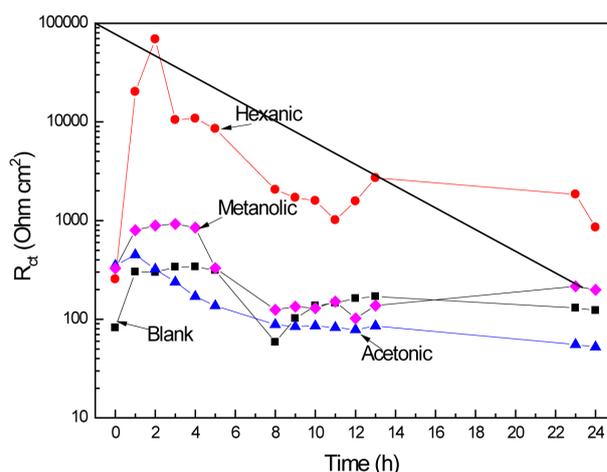
where  $f_{max}$  is the frequency value at which the imaginary component of the impedance is maximal. A  $C_{dl}$  value of 980 F  $\text{cm}^{-2}$  was found for the carbon steel electrode in the blank 0.5 M  $\text{H}_2\text{SO}_4$  solution and it decreases when the inhibitor is added. The double layer formed at the electrode-solution interface is considered as an electric capacitor, whose capacitance decreases due to the displacement of water molecules and other ions originally adsorbed on the electrode by the *Rosmarinus officinalis* molecules, forming a protective film [6,7]. The Nyquist plots shown for mild steel electrodes immersed in 0.5 M  $\text{H}_2\text{SO}_4$  solutions containing different concentrations of *Rosmarinus officinalis* in **Figures 8-10** depict a behavior analogous to that observed in solutions without the inhibitor, indicating that mainly a charge transfer process controls the corrosion of carbon steel. The thickness of the formed film increases with increasing concentrations of the inhibitor, since more *Rosmarinus officinalis* adsorbs on the surface, resulting in lower  $C_{dl}$  values. Such behavior and this data interpretation are in good agreement with previous reports on the inhibition of low carbon steel corrosion by succinic acid [39].

### 3.4. Extract Characterization

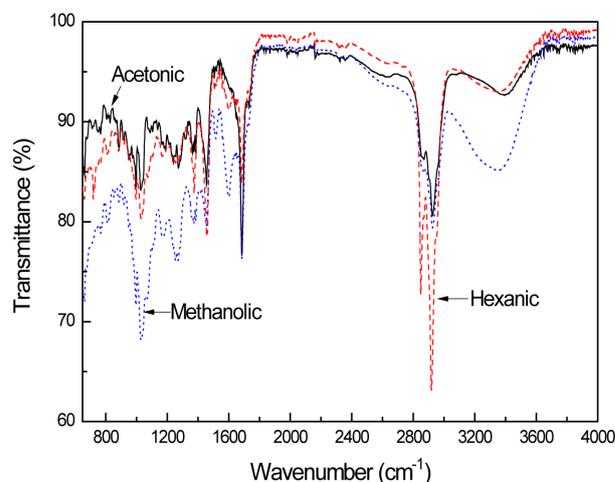
The infrared (IR) spectra for the different extracts, **Figure 14**, show that the main bands found for the total hexane extract are 3371  $\text{cm}^{-1}$ , assigned to the vibration of (O-H) bond. The presence of the hydroxyl group was assigned to the vibration of bond at 1684  $\text{cm}^{-1}$  corresponding to carbon-oxygen or carbonyl group (C=O); and one more vibration on 1016  $\text{cm}^{-1}$  due to a (C-O) single bond. These bands describe the carboxylic acid group; it



**Figure 12.** Variation of the Nyquist diagrams with time for carbon steel after 24 h of exposure to 0.5 M  $\text{H}_2\text{SO}_4$  with 1000 ppm of the hexanic extract of *Rosmarinus officinalis*.



**Figure 13.** Variation of the  $R_{ct}$  value with time for carbon steel after 24 h of exposure to 0.5 M  $\text{H}_2\text{SO}_4$  without and with 1000 ppm of *Rosmarinus officinalis*.



**Figure 14.** Infrared spectra of the different *Rosmarinus officinalis* extracts.

was confirmed that the vibration of  $1455.17\text{ cm}^{-1}$  corresponds to a (O-H) bond of carboxylic acid. At  $1370$  and  $1252\text{ cm}^{-1}$  the vibrations refers to (-C-CH<sub>3</sub>) bond and (C-H) vinylidene group. Other vibrations at  $1002$  and  $716\text{ cm}^{-1}$  showed the presence of (-CH-) and (-CH<sub>2</sub>-) groups respectively. It was found at  $1177$  and  $1031\text{ cm}^{-1}$  two vibrations which correspond to a (C-O) carbonyl conjugate aromatic ring and (C-O) for primary alcohol respectively. The non-polar extract of Rosemary contains several organic compounds as fatty oils, triglycerides, mono and diterpenes of natural products at rather different concentrations [40]. The hexanic extract is mainly made of compounds with saturated, aliphatic chains, however, it is also evident the presence of (O-H), (C-H) and (C=O) bonds, which suggests the presence of carboxylic acids. On the other hand, the acetonic and methanolic extracts are made mainly of carbonic, alcoholic (both primary and phenolic type and carboxylic groups, which contain in their structure (C-C) bonds, aromatic rings and (-CH<sub>2</sub>-) and (-CH<sub>3</sub>) groups. All these characteristics correspond to compounds such as flavonoids. Rosmarinic acid, carnosic acid and carnosol are the major bioactive constituents in rosemary leaves responsible for the antioxidant, anti-inflammatory, and anti-carcinogenic effect [26-28]. A number of flavonoids, including eriocitrin, hesperidin, diosmin, and homoplantagin have been identified from rosemary. The antioxidant activity of several flavonoids found in rosemary such as cirsimaritin and genkwanin has also been reported [41]. In the phenolic diterpenoid fraction of *Rosmarinus officinalis*, carnosic acid is the major component [25,40]. In addition, Bai *et al.* [42] isolated 15 new flavonoids, including rosmarinic acid, carnosol and carnosic acid that are responsible for the bioactivities on the basis of the reported anti-inflammatory and cancer preventive characteristics of rosemary. Thus, these results show that the inhibitory effect of *Rosmarinus officinalis* extract on the corrosion of 1018 carbon steel in  $0.5\text{ M H}_2\text{SO}_4$  is due to the presence of compounds such as flavonoids, passivating inhibitors that have been used satisfactorily in many corrosive environments [30,31].

#### 4. Conclusions

*Rosmarinus officinalis* extract has been proved to inhibit the corrosion of carbon steel in  $0.5\text{ M H}_2\text{SO}_4$  with its efficiency increasing with the extract concentration in the range between  $100 - 1000\text{ ppm}$ . Among the three different extract solvents, the hexanic extract showed a higher inhibition efficiency than that for the acetonic and methanolic. The inhibitive action of the extract was attributed to the adsorption of its components to the steel surface which followed a Frumkin adsorption isotherm. The chemisorption aspect of the adsorption process was well-established by the value of the adsorption free-

energy value of  $-37.4\text{ kJ}\cdot\text{mol}^{-1}$ . Polarization curves showed that the passivation current density value was substantially decreased by the addition of *Rosmarinus officinalis* extract. IR results indicated that the inhibitory effect of this extract is due to the presence of organic compounds such as flavonoids which act as passivating inhibitors.

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