A Study of Natural Rosmarinus Corrosion Inhibitor for Zinc
In HCl Solution

Haneen Faleh Wali¹, Shaker Salih Bahar²
¹,² Chemical Engineering Dep., Babylon University, Babylon, Iraq.
hanin.saad@student.uobabylon.edu.iq,shakersaleh617@yahoo.com

Abstract. In this study, the effect of important variables on the corrosion rate of Zinc metal was studied with free corrosion, weight loss, and polarization techniques. The test system was designed to measure corrosion potential, corrosion rate, limited current density, and the polarization technique. The experiment used a 0.1M HCl solution as its medium. Temperatures (20, 30, 40, 50, and 60) °C and rosemary inhibitor concentrations (1 and 5) g/L were used to study the efficacy of the zinc corrosion process. The results showed that the corrosion rate increased with increasing temperature but decreased with increasing inhibitor concentration in acid solution. The maximum inhibition efficiency in Weight Loss Experiments observed at 5g/L of rosemary and 20 °C is 49.07%. The corrosion potential became more negative with increasing temperature and became nobler (less negative) with increasing inhibitor concentration. It has been shown that rosemary is good as a green inhibitor in acid solution.

Keywords: Corrosion; Zinc metal; Rosemary; inhibitor; polarization.

1. Introduction
Corrosion is a metal's destructive attack on its environment caused by a chemical or electrochemical reaction. Metal corrosion wastes not just the metal, but also the energy, water, and human work that went into creating and fabricating the metal structures in the first place [1-3]. Zinc is one of the most often used metals, coming in fourth place behind iron, aluminum, and copper in terms of production and consumption worldwide. Zinc has a variety of applications, including galvanizing, die casting, and electronics. In high-energy-density batteries (such as Ni/Zn, Ag/Zn, and Zn/air), it is the preferred anode material. Acids have a high proclivity for attacking zinc. Figure (1) indicates that in acidic conditions, no surface oxides of zinc are stable, whereas zinc corrosion products are generated and are more stable under neutral or slightly alkaline circumstances. Hence, for scale removal and cleaning of zinc surfaces with acidic solutions, it becomes necessary to use inhibitors [4-6]. The use of inhibitors is one of the most practical methods by which to protect zinc from corrosion, particularly in acidic mediums [7]. Aloe vera extract [8], Citrullus vulgaris peel [9], mansoa alliacea plant extract [10], fenugreek [11], and natural onion juice [12] have all been reported as green corrosion inhibitors for Zn in various environments.
Plant extracts contain tannins, alkaloids, flavonoids, polyphenols, saponins, glycosides, anthraquinones, amino acids, proteins, and other heterocyclic compounds, among other phytochemical elements. These phytochemicals have been suggested as possible corrosion inhibitors [13]. The effectiveness of inhibition is achieved through one or more of the following mechanisms: preferential adsorption on anodic or cathodic sites and stopping the reaction, or the formation of a protective barrier film on the surface. The inhibitors are classed as anodic, cathodic, or mix-type based on their inhibition mechanism. Natural inhibitors have thus become a viable alternative to long-term technological advancement [14-17].

Rosmarinus officinalis l. (Rosemary) is an attractive evergreen shrub with pine needle-like leaves that grows wild in most Mediterranean regions. Rosemary essential oil is a widely used aromatic and medicinal plant with sterilizing, insecticidal, and anti-inflammatory properties. Perfume, bath liquid, cosmetics, shampoo, air freshener, ant repellent, and other everyday chemicals all include it. When it comes to spices, rosemary has a long history in the food industry [18-20]. Antioxidant, anti-inflammatory, antibacterial, anticancer, and antiandrogenic properties have been documented for the plant. Carnosol, carnosic acid, rosmanol, rosmadial, epirosmanol, rosmadinphenol, and rosmarinic acid are all phenolic compounds having inhibitory characteristics found in rosemary [21,22].

The corrosion inhibitory activity of Rosemary extract as a green inhibitor has previously been investigated in acid solutions on steel [23-30] and nickel [31]. To our knowledge, no research has been published on the inhibitory effects of rosemary extract on acid corrosion of zinc in hydrochloric acid solution. The effects of rosemary on zinc corrosion in a 0.1M HCl solution, as well as an open circuit and electrochemical polarization, were investigated in this study. It also takes into account the temperature.

2. Experimental work

2.1. Specimen Preparation

The working electrode is a sheet of zinc specimen (99.9% purity) with dimensions of 5 cm x 2 cm x 0.05 cm, which was used in the experiments as a cathode. The Zinc specimen was carefully and lightly polished with grit silicon carbide paper before each experiment, rinsed with water, cleaned in 3% HCl for 5 minutes, washed in tap water, dried with Gauze, and then dried in an electrical oven at about 110 °C for 10 minutes [32].

2.2. Inhibitor preparation

After drying the rosemary, it was ground with an electric grinder. This powder was weighed to the required weight (1.5 grams) before being immersed in one liter of water for 24 hours and filtered using a special filter paper.

2.3. Electrochemical Measurements

2.3.1. Weight Loss Experiments were achieved to determine the average corrosion rates under different inhibitor concentrations and temperatures. Using equations (1) and (2) below, corrosion inhibition efficiency (IE%) and the corrosion rate (gmd) were computed based on the measured corrosion current density [4]:

![Figure 1. Potential-pH equilibrium Pourbaix diagram for the zinc-water system at 25 °C](image)
Corrosion Rate \( (gmd) = \frac{\Delta W}{A t} \) \hspace{1cm} (1)

\[ i_a = \frac{\Delta w z F}{M \text{wt} A t} \times 10^6 \] \hspace{1cm} (2)

Typically, the inhibitor of the corrosion remains valued in terms of inhibition competence, and is given through the relationship [33]:

\[ IE\% = \frac{CR_o - CR_I}{CR_o} \times 100 \] \hspace{1cm} (3)

Anywhere CRA is the corrosion rate and the subscripts o and I mention toward the absence and presence of the inhibitor.

2.3.2. Free Corrosion Experiments: Electrochemical measurements were performed with two electrodes: a zinc specimen as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. After preparing the sample with previous steps and immersing it in a 0.1M HCl acid solution for 2 hours and using a voltmeter, the corrosion potential was determined at different temperatures and inhibitor concentrations.

2.3.3. Electrochemical Polarization Experiments to determine Ecorr corrosion current and corrosion potential using the Tafel method. Under different conditions, anode and cathode polarization curves were induced using three electrodes: zinc, SCE, and a graphite rod as an auxiliary electrode. The circuit was connected, and once all electrical connections were completed, the circuit was turned on, with a constant current source set to 10 volts. Record the reading of the voltage and the cathode current of the voltmeter and ammeter respectively, and cathodic curve can be plotted and then the anodic curve of polarization by substituting the anodic and cathodic connections. The corrosion parameters such as corrosion current (Icorr), corrosion potential (Ecorr), anodic Tafel slope (ba), and cathodic Tafel slope (bc) were calculated from the conducted polarization curves using the program Origin (data analysis software). The corrosion inhibition efficiency was calculated using Equation (4):

\[ IE\% = \frac{I_o - I_I}{I_o} \times 100 \] \hspace{1cm} (4)

Anywhere I is corrosion current density and the subscripts o and I mention toward the absence and presence of the inhibitor.

3. Results and Discussion

3.1. Discussion and Results of Weight Loss

The weight loss of zinc in a 0.1M HCl solution in the absence and presence of different rosemary concentrations and temperatures. The inhibitory efficiency, the rate of corrosion (gmd), and the values of dissolution current density (id) were calculated and given in Table (1). It can be shown in table (1) and Figure (2) that when the inhibitor concentration is increased, the corrosion rate is reduced. Adsorption of inhibitor results in the formation of bulky precipitates. Rosemary performs as an effective zinc corrosion inhibitor in hydrochloric acid solution, according to the findings. The efficiency of inhibition improves as the inhibitor concentration increases. His results show that increasing the extract concentration increases the number of inhibitor molecules adsorbed onto the zinc surface and decreases the surface area available for a direct acid attack. The presence of organic components in rosemary extract is thought to be responsible for its inhibitory impact. Rosemary contains a variety of chemicals.
Table 1. The result of Inhibitor rosemary Concentration & Temperature on Corrosion Rate of Zinc Specimen in 0.1M HCl solution at t= 2hr.

| T °C | C(g/L) Inhibitor | ∆W (g) | CR (gmd) | Id (μA/cm²) | Efficiency IE% |
|------|------------------|--------|----------|-------------|---------------|
| 20   | 0                | 0.0161 | 96.64    | 329.85      |               |
|      | 1                | 0.0100 | 60.02    | 204.88      | 37.89         |
|      | 5                | 0.0082 | 49.22    | 168.00      | 49.07         |
| 30   | 0                | 0.033  | 198.08   | 676.09      |               |
|      | 1                | 0.0203 | 121.85   | 415.90      | 38.48         |
|      | 5                | 0.0172 | 103.24   | 352.39      | 47.88         |
| 40   | 0                | 0.0646 | 387.76   | 1323.50     |               |
|      | 1                | 0.0419 | 251.50   | 858.43      | 35.14         |
|      | 5                | 0.035  | 210.08   | 717.07      | 45.82         |
| 50   | 0                | 0.0967 | 580.43   | 1981.16     |               |
|      | 1                | 0.0685 | 411.16   | 1403.40     | 29.16         |
|      | 5                | 0.0587 | 352.34   | 1202.63     | 39.30         |
| 60   | 0                | 0.1056 | 633.85   | 2163.50     |               |
|      | 1                | 0.0761 | 456.78   | 1559.11     | 27.94         |
|      | 5                | 0.0673 | 403.96   | 1378.82     | 36.27         |

Figure 2. Result of Inhibitor rosemary Concentration and Temperature on Zinc Corrosion Rate

3.2. Discussion and Results of Free Corrosion

From the figures (3, 4, 5) the potential behavior of zinc corrosion over time in HCl solution is shown under different conditions, and it can be seen that the potential becomes more negative with time. This behavior was due to the depletion of Oxygen due to its high drop on the surface of the metal. When the inhibitor concentration increased the potential became less negative.
Figure 3. Free corrosion of Zinc Specimen in 0.1M HCl solution without inhibitor.

Figure 4. Free corrosion of Zinc Specimen in 0.1M HCl solution with 1g/L of rosemary.

Figure 5. Free corrosion of Zinc Specimen in 0.1M HCl solution with 5 g/L of rosemary.

3.3. Discussion and Results of Polarization

Figures 6, 7, and 8 show the polarization curves for zinc in acid solution in the absence and presence of various Rosemary concentrations at various temperatures. The anodic and cathodic polarization curves shift to lower current densities when the inhibitor is added, according to the study. The polarization parameters; anodic Tafel slope (ba), cathodic Tafel slope (bc), corrosion potential (Ecorr), corrosion current (Icorr), and inhibition efficiency (IE%) are presented in Table (2). The data in Table (2) show that adding rosemary extract reduces the corrosion current density and that the corrosion potential shifts slightly to less negative values as the concentration of the added inhibitor is increased, and a large number of corrosion pits form on the surface of the zinc. This could be attributed to the adsorption of the inhibitor molecules on the metal's surface. It's also clear that as inhibitor concentrations rise, the IE% of rosemary extracts rise. The rosemary extracts had the highest inhibitory efficiency of 57.55. Instead, the general shape of the polarization curves is unaffected by temperature changes. These results suggest that rosemary has an inhibitory effect on zinc corrosion in an acidic medium, and that it works as a mixed inhibitor.
Figure 6. Polarization Curves of Zinc in 0.1M HCl without Inhibitor.

Figure 7. Polarization Curves of Zinc in 0.1M HCl with 1 g/l of rosemary Inhibitor.

Figure 8. Polarization Curves of Zinc in 0.1M HCl with 5g/l of rosemary Inhibitor.

Table 2. Polarization parameters for zinc in 0.1M HCl.

| T   | C(g/L) | Icorr (µA/cm²) | Ecorr (mV) | ba (mV/dec) | bc (mV/dec) | Efficiency IE% |
|-----|--------|----------------|------------|-------------|-------------|---------------|
| °C  | Inhibitor |             |            |             |             |               |
| 20  | 0      | 0.3978        | -675.297   | 179         | -298        |               |
| 1   | 0.2918 | -583.192      | 126        | -271        | 26.65       |               |
| 5   | 0.1903 | -622.312      | 134        | -176        | 52.16       |               |
| 30  | 0      | 0.6294        | -680.73    | 165         | -224        |               |
| 1   | 0.4262 | -672.881      | 123        | -199        | 32.28       |               |
| 5   | 0.2672 | -587.224      | 133        | -263        | 57.55       |               |
| 40  | 0      | 0.6522        | -629.582   | 189         | -339        |               |
3.4. FTIR Examination

FTIR spectra in the diversity of 4000–500 on behalf of the rare Rosmarinus remain exposed in Figure (9). FTIR spectral teaching documented the harmfully charged functional groups (hydroxyl, carboxyl, and amine) on the Rosmarinus surface. The whole band at 3383.26 cm\(^{-1}\) in unadulterated bark powder remains credited because of hydroxyl (-OH) stretching bands of alcohols and/or carboxylic acids vibrations or amine (-NH\(_2\)) stretching of polymeric complexes, followed by peaks of 2924.18 cm\(^{-1}\) and 2852.81 cm\(^{-1}\) assigned to vibration of the -CH\(_3\) asymmetric stretching and symmetric stretching absorption band of the methylene group vibration, respectively. Additionally, both peaks of 1741.78 cm\(^{-1}\) and 1651.12 cm\(^{-1}\) refer to the carbonyl group –C=O. Instead, the aromatic rings remain signified through the 1516.10 cm\(^{-1}\) whereas 1452.45 and 1375.29 cm\(^{-1}\) are associated with the –CH\(_3\) and C-O in phenols, respectively. 1269.20 cm\(^{-1}\) means the aromatic rings, though 1026.16 remains related through the (C-O) in phenols and (–CH\(_3\)) and the bands current underneath 825.56 remain fingerprint area of sulphur and phosphate functional groups. It is careful enough to leave an imprint on the Rosmarinus adsorbent around the presence of functional groups.

![FTIR Analysis](image)

Figure 9: FTIR analysis of natural Rosmarinus.

4. Conclusion

As obtained results have shown, rosemary (Rosmarinus) as the green inhibitor can be applied in order to reduce the corrosion rate of zinc in 0.1M HCl solution and it works as a mixed inhibitor. The inhibition efficiency was found to increase by increasing inhibitor concentrations and decrease with increasing temperature. In addition, the corrosion potential became less negative with increasing rosemary inhibitor concentration and became more negative with increasing temperature.
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