Corrosion Inhibition of Zinc Metal in 2M Hydrochloric Acid Solution by Using GuaifenesinDrug as an Inhibitor and Theoretical Calculations

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Abstract

The inhibition of the corrosion of Zinc in 2 M HCl by guaifenesin has been investigated at room temperature using weight loss measurements. Results obtained showed that guaifenesin is a good inhibitor and its inhibition efficiency (IE %) increased with the increase of inhibitor concentration since it was 81%. At 300 ppm.

The surface coverage was 0.81 at 300 ppm inhibitor concentration; hence the optimum concentration was 300 ppm.

Theoretical calculations investigate by studying the relationship between molecular structure and inhibition efficiency by using semi-empirical molecular quantum calculations within the PM3 method as implemented in HyperChem package.

Keywords**:** Inhibition efficiency; Zinc metal; guaifenesin; surface coverage.

1.Introduction

Zinc is an active metal with numerous industrial applications and is mainly used for the corrosion protection of steel. The zinc coated steel materials provide a greater resistance to corrosion but when exposed to humid atmosphere, they undergo rapid corrosion with the formation of a corrosion product known as white rust[1]. The formation of white rust is generally observed in galvanized materials and renders the plated zinc materials unsuitable for industrial applications. Also, industrial processes such as scale removal and cleaning of zinc surfaces with acidic solutions expose zinc to corrosion. Therefore, in order to protect the metal from corrosion, the use of inhibitors is necessary [2]. To reduce corrosion must use corrosion inhibitor; a corrosion inhibitor is a chemical compound which is designed to protect a metal or alloy from corrosion. While corrosion inhibitors will not halt or completely prevent corrosion, they can reduce the rate at which corrosion occurs, and block early corrosion damage. A wide variety of chemicals can be used for this purpose, although many are toxic, and must therefore be used with care to protect the environment [3,4]. We choose some drugs as corrosion inhibitors because drug molecules contain oxygen, nitrogen and sulphur as active centers, drugs are reportedly environmentally friendly and important in biological reaction, anddrugs can be easily produced and purified [5,6]. Theoretical treatment of the formation of compound in the gas phase, this was done using the hyperchem-7 program for the Molecular mechanics and semi- empirical calculations. Semi-empirical methods use parameters derived from experimental values that simplify theoretical calculations. These methods usually do not require long computation times, and lead to qualitative descriptions of molecular systems. In particular, the semi-empirical PM3 method makes uses of an accurate procedure to predict chemical properties, through a simplified Hartree-Fock (HF) Hamiltonian [7]. The correlation between theoretically calculated properties and experimentally determined inhibition efficiencies has been studied successfully for uniform corrosion [8].

2.Experimental Part

Zinc strips of BDH grade was used in dimension (8cm*2cm *0.5mm) (length, width, and thickness), scrubbed with emery paper, and washed with acetone several times, and a solution of 2M HCl was prepared. Guaifenesin inhibitor was prepared in 500 ppm concentration, thereafter subsequent dilution was employed to prepare solutions 400, 300, 200, and 100 ppm. Zinc strip was immersed in 2M HCl solution in absence of inhibitor for specific periods of time and

weighed in electronic balance after each period.

Weight loss measurements:

For weight loss measurements, the following formulae were employed

$$\Delta m = (m_1 - m_2) \quad \text{.....(1)}$$

Where m_1 and m_2 are the weights of metal before and after exposure to the corrosive solution, respectively.

The corrosion rate, the percentage of inhibition efficiency (IE %) and the degree of surface coverage (θ) of the investigated compounds was calculated from the following equations [9].

$$\text{Corrosionrate} = \Delta m / \Delta t \quad \text{.....(2)}$$

$$IE\ \% = [1 - (\Delta m_{inh} / \Delta m_{free})] \times 100 \quad \text{.....(3)}$$

$$\theta = [1 - (\Delta m_{inh} / \Delta m_{free})] \quad \text{.....(4)}$$

Where Δm_{free} and Δm_{inh} are the weight losses in the absence and presence of inhibitor, respectively.

Theoretical calculations:

Theoretical calculations were carried out using the semi-empirical calculations with PM3 method For this purpose the Hyperchem Program with complete geometry optimization was used. The purpose of these calculations is to provide information about the electron configuration of several organic inhibitors by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency. Some electronic properties such as energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) between LUMO and HOMO and Mulliken charges on the backbone atoms for prepared molecule [**7**] were planned to determine.

3. Results and Discussion

The corrosion of zinc strips in hydrochloric acid was studied by weight loss measurements using equations (1),(2), and the corrosion rates (g/min) of zinc were plotted against time (min) and as shown below in Fig.(1).

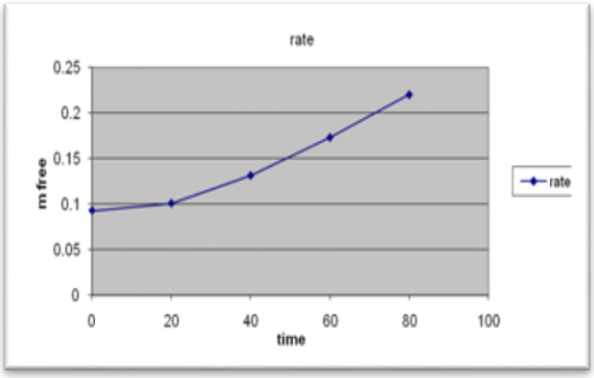


Fig.(1) Weight loss vs. immersion time for Zn strip in 2M HCl without inhibitor at 25°C.

The corrosion inhibitor is a chemical substance that interacts with the metal surface by an adsorption process protecting metal surface by forming film [9,10]. Inhibitor retards the corrosion either by reducing the movement or diffusion of ions to the metal surface, or by increasing the electrical resistance of metallic surface [11]. The inhibitor molecules could be adsorbed on the metal surface, so the aromatic nuclei and the oxygen atoms provides electrons that are needed to retard the formation of zinc ions, and the coating of zinc strips depends on how much the surface can accommodate the guaifenesin molecules, and the presence of this inhibitor induces chemical bonds with Zinc surface. These chemical bonds increased with increase of the inhibitor concentrations. Fig.(2) showed that the lowest corrosion rate was at 300 ppm, so it is the optimum concentration for inhibition, and this is might be attributed to the maximum coating of zinc strips at this concentration, and the guaifenesin molecules are distributed homogenously on the surface of zinc strips, and at 300 ppm the accommodation of guaifenesin molecules on the surface of zinc strips might be relatively non-homogeneous. The surface coverage θ, of the zinc strips by the adsorbed inhibitor was calculated from weight loss measurements using equation (4).

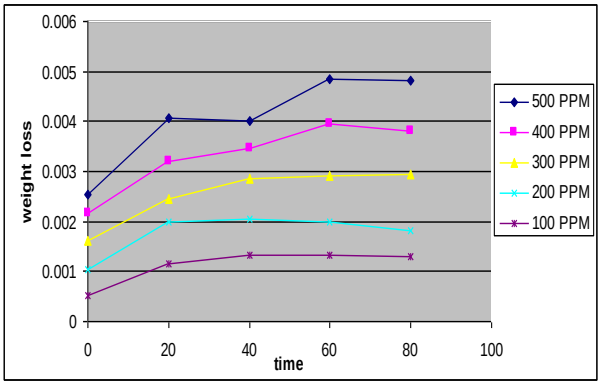


Fig. (2) Weight loss vs. immersion time for Zn strip in 2M HCl in presence of inhibitor at (500, 400, 300, 200 and 100) ppm of inhibitor.

The maximum surface coverage was found to be at 300 ppm, and this is could be attributed to the moderate concentration and the molecules of guaifenesin at this concentration diffuse from the bulk solution into the surface of zinc to cover it and inhibit the corrosion.

Table (1)
Measure of weight loss and calculate (θ, IE%, and rate of corrosion) in presence of inhibitor.

IE% 500ppm	*IE% 400ppm*	*IE% 300ppm*	*IE% 200ppm*	*IE% 100ppm*
73.56	75.28	81.32	80.93	77.12
46.20	56.26	65.82	74.68	75.44
44.73	50.98	59.07	75.65	79.43
48.40	57.87	69.14	80.44	75.48
42.25	38.71	45.96	75.80	78.06

The inhibition efficiencies increased as inhibitor concentration increased, at 300 ppm the inhibition efficiency was the maximum and it was 81%. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface.

Theoretical calculations

The purpose of theoretical study is to provide information about the electron configuration of several organic inhibitors by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency. All the calculations for geometry optimization were performed using the semi-empirical calculations with PM3 method. This computational method has been proven to yield satisfactory results [12,13].

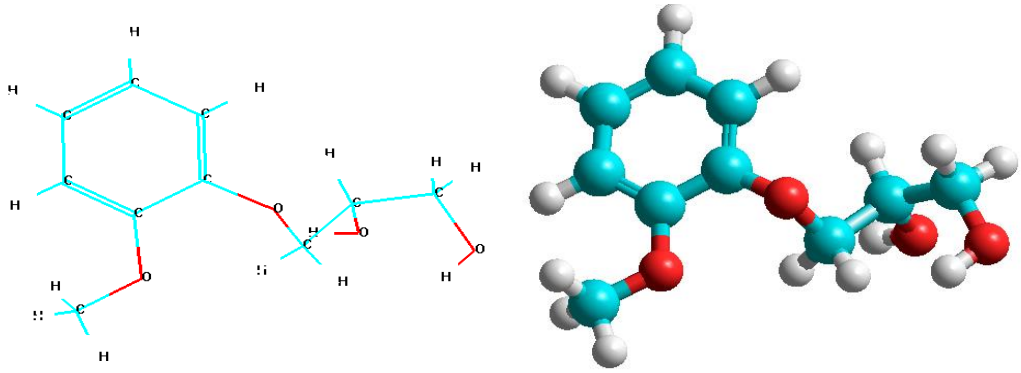
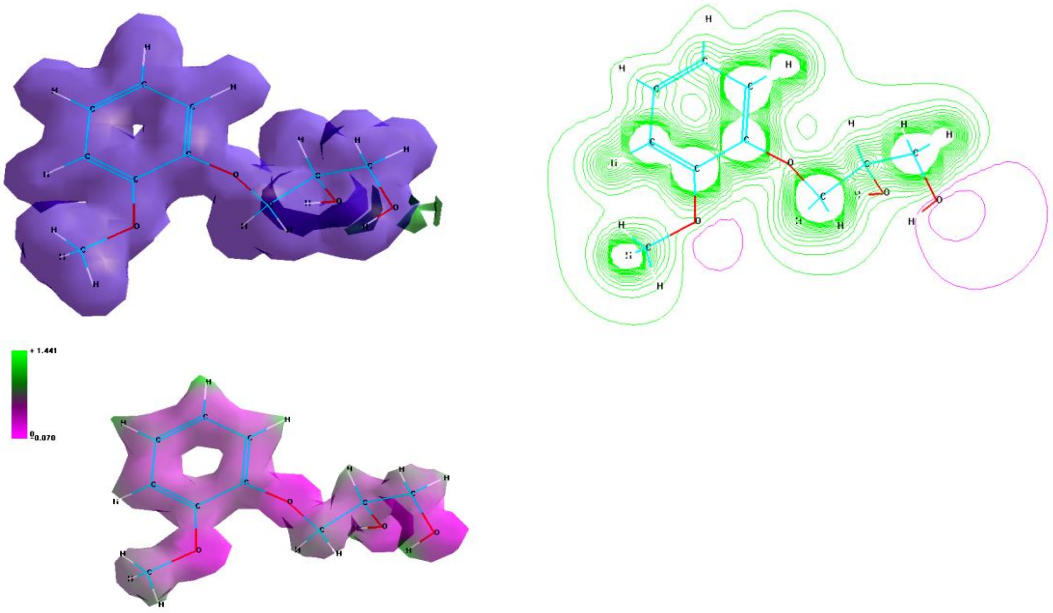


Fig.(3) Structure of guaifenesin.

The easiest way to compare the inhibition efficiency of compound is to analyze the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The calculated energies E_{HOMO}, E_{LUMO}, energy gap ($\Delta E=E_{LUMO}-E_{HOMO}$) and other indices are given in Table (2).



ELECTROSTATIC (2D&3D)

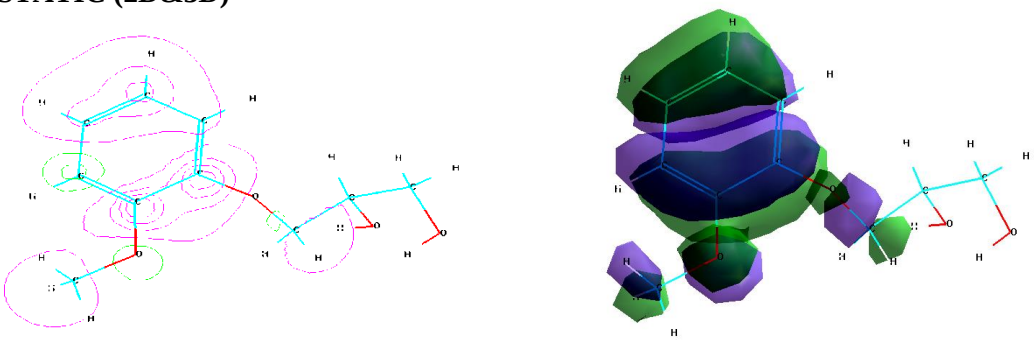


Fig. (4) HOMO and LUMO as 2D&3D Contours for guaifenesin.

Table (2)
Calculated quantum chemical parameters of prepared compound as modeling systems by using PM3 method.

ENERGIES AND GRADIENT

Total Energy	*-59376.6731777 (kcal/mol)*	*Total Energy*	*-94.620862496 (a.u.)*
Binding Energy	**-2815.1890877 (kcal/mol)**	**Isolated Atomic Energy**	**-56561.4840900 (kcal/mol)**
Electronic Energy	**-337218.6650972 (kcal/mol)**	**Core-Core Interaction**	**277841.9919195 (kcal/mol)**
Heat of Formation	**-138.6250877 (kcal/mol)**	**Gradient**	**0.0733464 (kcal/mol/Ang)**
MOLECULAR POINT GROUP	**C1**	**Dipole Moment**	**4.575 D**
HOMO	**-9.338441 ev**	**LUMO**	**-0.06126637 ev**
Total Energy	**-89607.2859172 (kcal/mol**	**Total Energy**	**-142.795448542 (a.u.)**
Binding Energy	**-3378.7477672 (kcal/mol)**	**Isolated Atomic Energy**	**-86228.5381500 (kcal/mol)**
Electronic Energy	**-572819.6000362 (kcal/mol)**	**Core-Core Interaction**	**483212.3141190 (kcal/mol)**
Heat of Formation	**-135.7607672 (kcal/mol)**	**Gradient**	**0.0927080 (kcal/mol/Ang)**
MOLECULAR POINT GROUP	**C1**	**Dipole Moment**	**6.683 D**
HOMO	**-9.40832 ev**	**LUMO**	**-1.082552 ev**

The energy gap (ΔE) between the HOMO and LUMO energy levels of the molecules is important factor, whereas, low absolute value of the energy gap (ΔE) gives good inhibition efficiencies [14]. The compound showed lowest energy gap that in good agreement experimental results (see Table (2)).

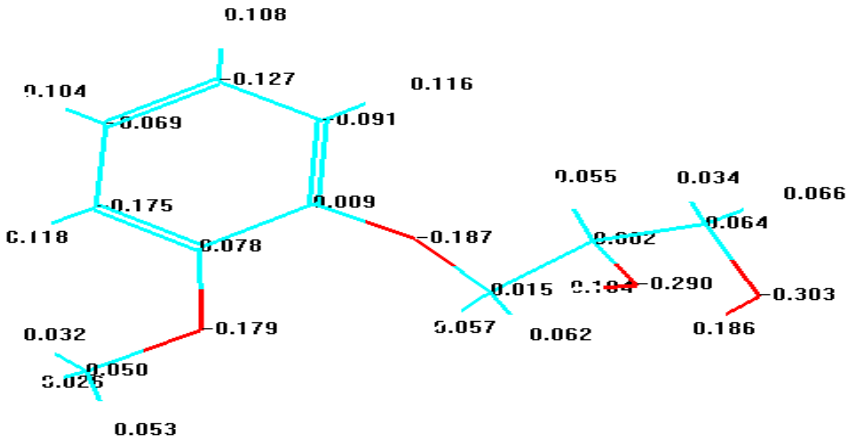


Fig. (5) Formal charges of guaifenesin.

3.Conclusions

The guaifenesin drug was used to inhibit the corrosion of zinc, and the inhibition efficiency was found to be maximum at 300 ppm concentration of inhibitor. The maximum surface coverage was found to be maximum at 300 ppm inhibitor concentration which means that the maximum adsorption was at this concentration, and the molecules of guaifenesin drug have formed a thin film

which prevents the penetration of acid into the surface of zinc. Theoretical calculations were used as useful tools to investigate the relationship between molecular structure and inhibition efficiency by using semi-empirical molecular quantum calculations within the PM3 method.

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الخلاصة

تم دراسة تثبيط تآكل معدن الخارصين في محلول 2 مولاري من حامض الهيدروكلوريك وفي درجة حرارة الغرفة باستخدام طريقة تناقص الوزن، وقد تم تثبيط تآكل الخارصين باستخدام دواء كوايفينيسين وقد بينت الدراسة ان هذا الدواء هو مثبط جيد وان نسبة كفاءة التثبيط قد ازدادت بازدياد تركيز المثبط. حيث كانت افضل تغطية سطحية للمثبط عند تركيز 300 جزء من المليون ولقد تم دراسة العلاقة بين التركيب الجزيئي وبين كفاءة التثبيط باستخدام بعض الحسابات النظرية.