Short Communication

Furosemide as an Environmental-Friendly Inhibitor of Corrosion of Zinc metal in Acid Medium: Experimental and Theoretical studies

Emad Yousif [1,], Yip-Foo Win[2], Ali H. Al-Hamadani[3], Ahmed A. Al-Amiery[3,4,*], Abdul Amir H. Kadhum[4], Abu Bakar Mohamad[4]*

[1] Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq
[2] Faculty of Science, Universiti Tunku Abdul Rahman, Perak Campus, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
[3] University of Technology, Baghdad 10066, Iraq
[4] Department of Chemical and Processing Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Bangi, Selangor 43600, Malaysia
[*]E-mail: dr.ahmed1975@gmail.com

The anticorrosion ability of Furosemide (4-chloro-2-(furan-2-ylmethylamino)- 5-sulfamoylbenzoic acid). was tested on Zinc metal (ZM) in 2 M HCl media by a weight loss method at various concentrations. The results indicated that inhibition efficiencies were enhanced with an increase in concentration of Furosemide and it shows the highest inhibition efficiency of 81.32% at 300 ppm. The theoretical correlation of molecular structure and inhibition efficiency of Furosemide has been carried out by using semi-empirical Hamiltonian calculations based on Parametrized Model 3 (PM3).

1. INTRODUCTION

In general, a corrosion inhibitor is a chemical that interacts well with the metal surface by an adsorption process to form a thin film/layer to protect the metal surface by reducing the movement/diffusion of ions to the metal surface or by increasing the electrical resistance of metallic surface [1-3]. Zinc is an active metal with vast industrial applications and mainly used for the corrosion protection of steel. However, zinc corroded when exposed to humid atmosphere, industrial environment and aqueous media and form a white layer known as white rust [4]. Normally the white rust is observed in galvanized materials and its occurrence remains as a serious commercial problem. Control or slow down the formation of white rust; the search for new inhibitors is essential [5]. A

significant method to protect the metals from corrosion is by addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. To this end, the use of organic compounds containing nitrogen, oxygen, and/or sulfur in a conjugated system as inhibitors to reduce corrosion attack has received detailed attention [6-15]. These compounds act at the interphase created by corrosion product between the metal and aqueous aggressive solution and their interaction with the corroding metal surface, usually via adsorption, often leads to a modification in either the mechanism of the electrochemical process at the double layer or in the surface available to the process. In recent years, being focused on green chemistry using environmentally benign reagents and conditions is one of the most fascinating developments in the synthesis of widely used organic compounds. Multicomponent domino reactions (MDRs) [16−18] particularly those performed in aqueous media, have become an increasingly useful tool for the synthesis of chemically and biologically important compounds because of their convergence, atom economy, and other suitable characteristics from the point of view of green chemistry [19-21]. In the earlier work, a large number of organic compounds have been studied and tested as an inhibitor and have been found to be not environmental friendly [22]. Hence, new and environmental friendly chemicals have to be explored to balance between industrial and environment need. The choice of compounds that used as corrosion inhibitors should be based [23] on the following criteria; first electronegative atoms such as oxygen, nitrogen and sulphur as an active center, second, environmentally friendly and important in biological reaction, and third easily produced and purified [24]. Organic and inorganic additives which prevent the adsorption of Cl ions and/or by the formation of a more resistant oxide film on the metal surface [25]. Of the most important and efficient acid inhibitors are organic compounds containing mainly nitrogen, oxygen, phosphorus and/or sulphur in their structures. The extent of inhibition by these compounds depends on the effective organic group and increases in the order: oxygen < nitrogen < sulphur < phosphorus [26,27]. Various organic compounds are reported as good corrosion inhibitors in hydrochloric acid media [28–34]. The inhibition efficiency of these compounds depends mainly on the structure and the nature of the adsorbed layer on the metal surface [35–37]. To further understand about qualitative structure-activity relationship (QSAR) of certain compounds as an inhibitor, theoretical study by using semi-empirical Hamiltonian calculations based on Parametrized Model 3 (PM3) were employed. In fact, with the aid of theoretical study an accurate prediction of chemical properties through a simplified Hartree-Fock method, the correlation between theoretically and experimentally determination of inhibition efficiency (%I.E.) would be a value-added information [38,39]. In this present study is aimed to investigate the inhibition efficiency (%I.E.) and the theoretical correlation of molecular structure of Furosemide as an inhibitor for the corrosion of zinc in HCl.

2. EXPERIMENTAL

2.1. Weight loss method

Zinc strips having rectangular shape with the surface dimension of 8.0 x 2.0 x 0.5 cm were obtained from BDH Merck Ltd. The strips were degreased with trichloroethylene and scrubbed with

different grades of emery paper. Then, washed with deionized water and rinsed with acetone for three times. The dried strips were weighed and immersed in 100 cm^3 of 2.0 M HCl solutions without Furosemide as an inhibitor for 80 minutes at 298 K. The subsequent study was carried out by immersing the zinc strips into solutions containing 500, 400, 300, 200 and 100 ppm of Furosemide . The different in weight was taken as the weight loss of zinc and the inhibition efficiency (%I.E.), corrosion rate (CR) as well as surface coverage (θ) of zinc strips were calculated by following equations respectively.

$$\Delta m = (m_1 - m_2) \text{ ----------------------------- (1)}$$
$$CR = \Delta m/\Delta t \text{ ------------------------------- (2)}$$
$$\%IE = [1 - (\Delta m_{inh}/\Delta m_{free})] \times 100 \text{ ------ (3)}$$
$$\theta = [1-(\Delta m_{inh}/\Delta m_{free})] \text{ -------------------- (4)}$$

where m_1 and m_2 are the weights of zinc strips before and after exposure to the corrosive solution; Δm_{free} and Δm_{inh} are the weight losses in the absence and presence of inhibitor, respectively.

2.2. Theoretical calculations

Theoretical calculations were carried out by using the semi-empirical Hamiltonian calculations based on Parametrized Model 3 (PM3). In this study, HyperChem 7 Programme with complete geometry optimization was used to provide information about the electron configuration of several organic inhibitors by quantum chemical calculations to investigate the relationship between molecular structure and inhibition efficiency. The electronic properties such as energy of the Highest Occupied Molecular Orbital (E_{HOMO}), Lowest Unoccupied Molecular Orbital (E_{LUMO}), energy gap (ΔE) and Mulliken charge on the backbone atoms of Furosemide was determined [40].
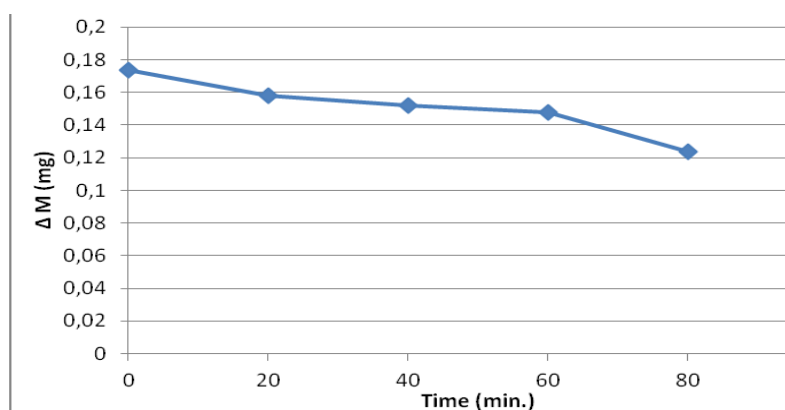

3. RESULT AND DISCUSSION

Figure 1. Weight loss versus immersion time for Zn strip in 2.0 M HCl without inhibitor at 298K.
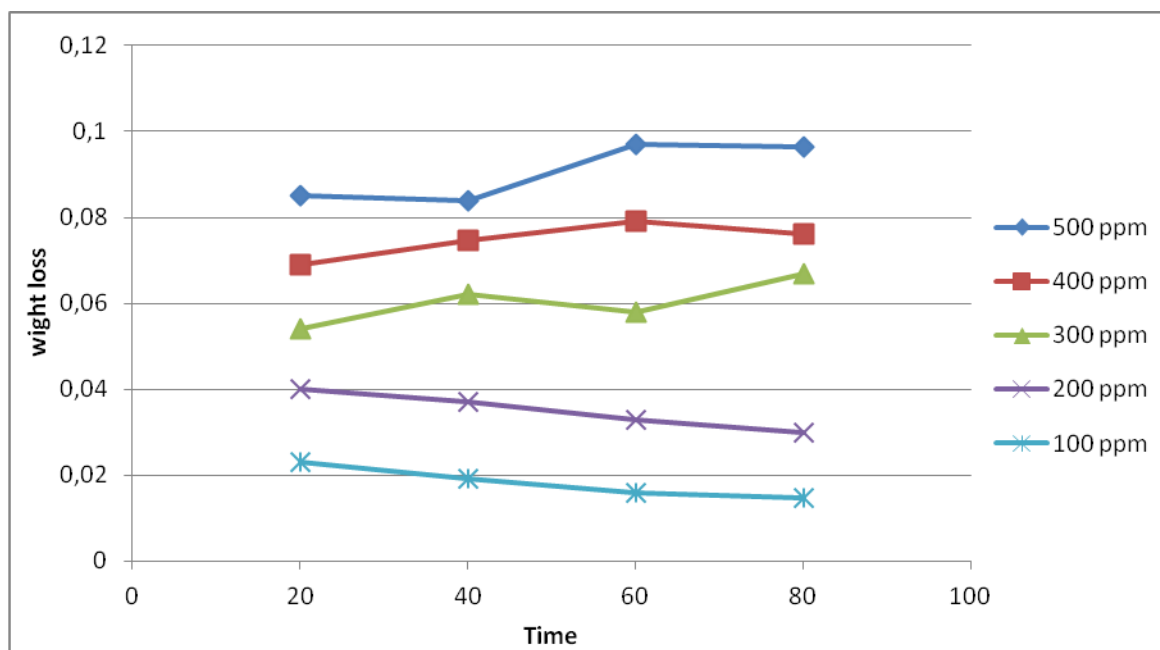
Figure 2. Weight loss versus immersion time for Zn strip in 2.0 M HCl in presence of 500, 400, 300, 200 and 100 ppm of Furosemide .

The corrosion of zinc strips in hydrochloric acid was studied by weight loss method and the calculations were based on equations (1) and (2). The corrosion rate (mg/min) of zinc with and without Furosemide is shown in Figures 1 and 2 respectively. As usual, the zinc strips going to be thinner from time to time until 80 minutes indicating the corrosion took place when zinc strips immersed in the hydrochloric acid without any inhibitors. In this study, the lowest corrosion rate of Furosemide was found at 300 ppm as an optimum concentration of Furosemide. Based on the calculation of surface coverage (θ) (not shown) and inhibition efficiency (%I.E.), the maximum θ also found at 300 ppm with the highest %I.E. value of 81.32% (refer to Table 1).

Table 1. Measurement of weight loss and calculation of %IE in the presence of Furosemide

%IE 500 ppm	%IE 400 ppm	%IE 300 ppm	%IE 200 ppm	%IE 100 ppm
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

It was believed that at optimum concentration of 300 ppm, the Furosemide molecules diffused from bulk solution and distributed homogeneously onto the zinc surface to form an optimum coating which acted as a protective layer to inhibit the corrosion processes. In addition, at the zinc surface, the aromatic and oxygen atoms of Furosemide might provide sufficient electrons that are needed to retard the formation of zinc ions which in turn to slow down or inhibit the corrosion processes. Figures 3-4

showed the 2D and 3D contours and Figure 5 showed the formal charges of Furosemide molecule respectively. All the figures were obtained from the computational methods and theoretical calculations as mentioned earlier. In addition, all the calculated quantum chemical parameters of Furosemide molecule are given in Table 2.
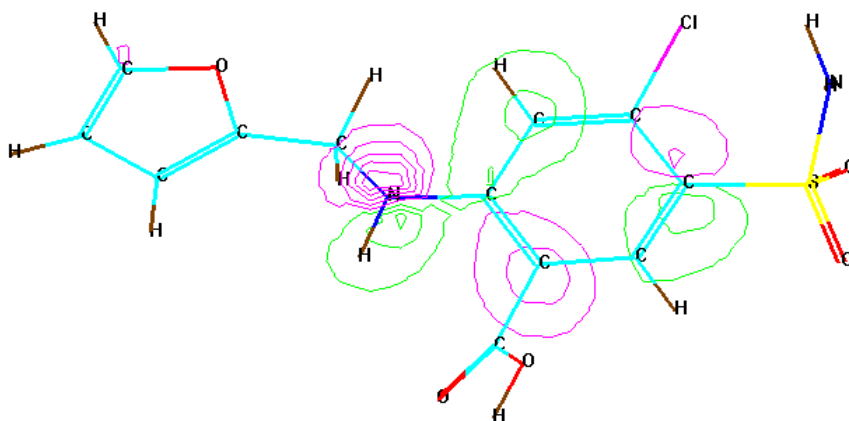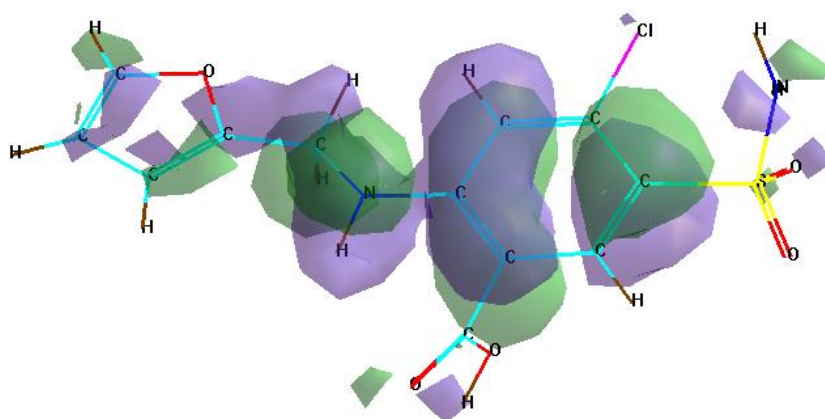

Figure 3. HOMO and LUMO in 2D contours of Furosemide.

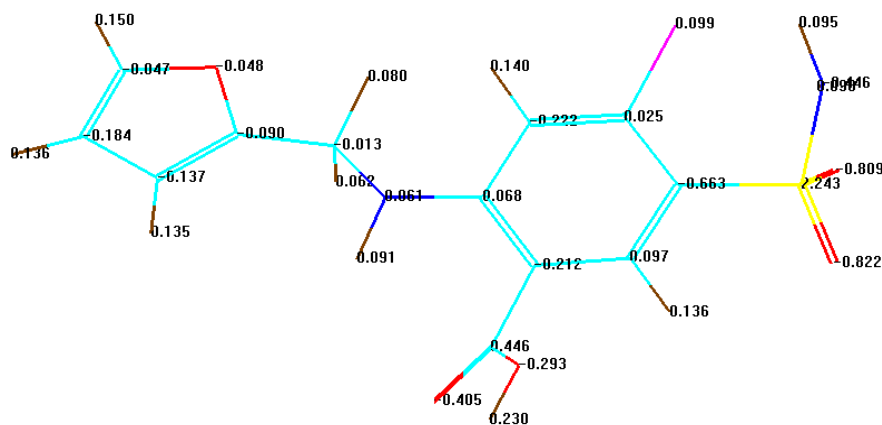**Figure 4.** HOMO and LUMO in 3D contours of Furosemide.

Figure 5. Formal charge of Furosemide

Table 2. Calculated quantum chemical parameters of Furosemide as modeling systems by using Parametrized Model 3, PM3.

Energy/gradient	Value
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)

Recently, theoretical studies has been used to analyze the characteristics of the inhibitor/ surface mechanism and to describe the structural nature of the inhibitor in the corrosion process as well as analyze the experimental data. It has been found to be successful in providing insights into the chemical reactivity and selectivity in terms of global parameters the choosing of the Furosemide for use as a corrosion inhibitor due to contains oxygen, sulfur and nitrogen atoms as active centers. It is well established in the literature that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied d orbital of the metal, and the higher the corrosion inhibition efficiency. In addition, the lower the LUMO energy, as the LUMO–HOMO energy gap decreased and the efficiency of inhibitor improved. E_{HOMO} is often associated with the electron donating ability of a Furosemide. Therefore, increasing values of E_{HOMO} indicate a higher tendency for the donation of electron(s) to the appropriate acceptor molecule with low energy and an empty molecular orbital. Increasing values of E_{HOMO} thus facilitate the adsorption of the inhibitor. Consequently, improving the transport process through the adsorbed layer would enhance the inhibition efficiency of the inhibitor. This finding can be explained as follows. E_{LUMO} indicates the ability of the molecule to accept electrons; therefore, a lower value of E_{LUMO} more clearly indicates that the molecule would accept electrons [41]. HOMO (Figure 3 and 4) is often associated with the electron donating ability of an inhibitor molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to a metal with unoccupied molecule orbitals. E_{LUMO}, conversely, indicates the ability of the molecule to accept electrons [42]. A lower value of E_{LUMO} indicates an easier acceptance of electrons from a metal surface [43]. The gap between the LUMO and HOMO energy levels of inhibitor molecules is another important parameter. Low absolute values of the energy band gap ($E = E_{LUMO} - E_{HOMO}$) mean good inhibition efficiency [44]. Consequently, we can conclude that the corrosion inhibition efficiency becomes better when the system is characterized by high values of the electronic chemical potential, HOMO energy, LUMO energy, nucleophilicity and low values of the HOMO-LUMO energy gap. The IE% increases when E_{HOMO} increase and when the E_{HOMO}-E_{LUMO} gap decreases. Therefore, Furosemide is better corrosion inhibitor. From the computational method and theoretical calculations, the $\Delta E = E_{LUMO} - E_{HOMO}$ value showed a low absolute reading indicating Furosemide molecule possessed a good %I.E [45-49]. As a preliminary stage, the theoretical study was in good agreement with the experimental result which inspired for the further in depth study on Furosemide as a corrosion inhibitor.

4. CONCLUSION

Study the corrosion inhibition of Zinc in 2.0 M HCl solutions at 30 ^{o}C using Furosemide as an inhibitor in concentrations of 100, 200, 300, 400 and 500 ppm. Furosemide exhibited excellent inhibition performance optimum concentration 300 ppm. In general, the acidic corrosion of Metals was reduced by the addition of an appropriate concentration, but our inhibitor has optimum concentration at 300 ppm. The inhibition efficiencies increased with inhibitor concentration until the optimum concentration, but were reduced proportionally with concentration higher than the optimum. The inhibition efficiencies obtained by using of weight loss method. Furosemide molecule showed that the highest %I.E. at optimum concentration of 300 ppm with the maximum θ. Based on the theoretical calculations, the low absolute reading of ΔE indicating that Furosemide molecule possessed a good %I.E. which in good agreement with the experimental study. Hence, further in depth study on surface morphology, influence of pH and etc parameters will carry out to explore the inhibition mechanism of Furosemide molecule.

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