Study of Corrosion Inhibition for Mild Steel in Hydrochloric Acid Solution by a new furan derivative

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Abstract. The corrosion inhibition effect of a new furan derivative (furan-2-ylmethyl sulfanyl acetic acid furan-2-ylmethylenehydrazide) on mild steel in 1.0 M HCl was investigated using corrosion potential (ECORR) and potentiodynamic polarization. The obtained results indicated that the new furan derivative (furan-2-ylmethyl sulfanyl acetic acid furan-2-ylmethylenehydrazide) (FSFD) has a promising inhibitive effects on the corrosion of mild steel in 1.0 M HCl across all of the conditions examined. The density functional theory (DFT) study was performed on the new furan derivative (FSFD) at the B3LYP/6-311G (d,p) basis set level to explore the relation between their inhibition efficiency and molecular electronic structure. The final experimental results showed that FSFD act as a good corrosion inhibitor in the acidic solution for mild steel which is in agreement with the results of the theoretical study.

Keywords: Furan derivative, FSFD, Mild Steel, Corrosion inhibitor.

1. Introduction

Corrosion is a fundamental property of metals and alloys in an acidic or saline solution. Studies on corrosion represent a growing field due to substantial financial losses in various sectors and require extensive efforts to limit its impact [1-3]. Recent years have witnessed a growing academic interest in studies on inhibitor corrosion in many ways. Corrosion inhibitor is an increasingly important area particularly in industria [4-6]. Recent years have shown interest in using organic compounds containing sulfur, oxygen, and nitrogen atoms to inhibit corrosion process [7-9]. Organic compounds with heteroatoms are among the most widely used in inhibitor corrosion due to the effect of the polar groups and Pi-electrons on the iron surface and minimizing the effect of corrosion [10-11]. In this work, we used a new furan derivative FSFD with molecular formula (C12O3N2S12H12) as show in Figure 1. FSFD was synthesized and characterized by Luma S.A. [12]. A new furan derivative was applied as corrosion inhibitor by investigated in the mild steel in acidic solution (1.0 M HCl) with different concentrations using electrochemical measurements and theoretical treatment using Gaussian 05 in two media (vacuum and ethanol solvent).
Figure 1. Structure of (furan-2-ylmethyl sulfanyl acetic acid furan-2-ylmethylenehydrazide)

2. Experimental

2.1 Preparation of carbon steel sample

Mild steel which has the configuration percentages as shown in Table 1 was used.

| Metal | Amount |
|-------|--------|
| Fe%   | 99.579 |
| S%    | 0.0154 |
| Cu%   | 0.065  |
| Mn%   | 2.88   |
| Zn%   | 99.989 |

Table 1. Structure of carbon steel [13].

The sample of mild steel was subjected to surface cleaning by absolute ethanol and drying in acetone. The specimen material was fabricated in circular samples with dimensions of 2.5 cm in diameter and used as working electrode.

2.2 Preparation solutions

2.2.1 Blank solution

Corrosive solution (1.0 M HCl) was prepared. Dilution of analytical grade 35.4% HCl with purified water up to 1 liter. Blank solution consisted of 990 ml of 1.0 M HCl and completed to 1 L with 10 ml ethanol solvent.

2.2.2 Corrosion Inhibitor FSFD solution

Three different concentrations (100, 200, 300 ppm) were prepared by dissolving FSFD powder in the ethanol solvent and transferred to a volumetric flask of 10 ml.

2.3 Corrosion Potential (ECORR) Measurements

The electrochemical system consisting of a potentiostate, three electrodes, with a controlled computer and standard corrosion cell was used. The thermostat was among the most widely used to control the temperature of (1.0 M HCl) which flows through the external vessel at 30°C. Figure 2 shows the corrosion cell, and the three electrodes were:

1-The first is the reference electrodes which based on its potential consist of AgCl, Ag, KCl, and the outer solution filled with the prepared hydrochloric acid solution (1.0 M HCl). The reference electrode, a lugging tube placed at the distance 2mm from working electrode.
2- The second electrode is auxiliary consists of high purity platinum rod with 0.6 mm in diameter and 10 cm in length.
3- The third is working electrode (mild steel) which was mounted in the working electrode load with 1 cm² surface area the opening uncovered to the acidic solution.

![Figure 2. (a) The corrosion cell and the three electrodes. (b) Experimental set up.](image)

2.4 Experimental Procedure
The corrosion rate calculation protocol was carried out in compliance with the following steps:

1- One liter of corrosive media has been applied to the corrosion cell (see paragraph 2.3).
2- The temperature of the solution has been raised to the desired value with the use of the circulator of the water bath.
3- The first programmed step in this measurement is the open-circuit potential and the polarization curve starts at an open-circuit potential of approximately ± 200 mV from the open-circuit.
4- Measurements of corrosion for mild steel were assessed at 1.0 M. HCl with potentiostatic and blank solution followed by an inhibitor at different concentrations.
5- Corrosion current density (I mA) and corrosion potential (E mV) are calculated from the polarization curve as seen in Table (2) and in Figures (3-5).

3. Results and Discussion
3.1 Potentiostatic Polarization Measurement
In order to investigate the effects of electronic structure of FSFD compound as inhibitor corrosion, the theoretical study was conducted for FSFD compound [14]. The potentiostatic polarization curves for mild steel without and with FSFD immersed in 1.0 M HCl solution at temperatures range 303K are show in Figures 3, 4, 5 and the results are listed in Table 2.
Table 2. Polarization parameters for different concentrations of the FSFD at mild steel in acidic solution at 303 K.

| Conc (ppm) | Ecorr.(Mv) | Icorr.(µA.cm²) | -bc (mV/Dec) | ba (mV/Dec) | W(Lg.m².d⁻¹ P(Lmm.y⁻¹) | Rp(Ω.cm²) | IE% | CR (mpy) |
|-----------|------------|----------------|--------------|-------------|----------------------|----------|-----|---------|
| 0         | 490.1      | 872.24         | 87.5         | 100.2       | 12.45                | 3.44     | 23  | 0       | 403     |
| 100       | 467.1      | 410.46         | 86.4         | 88.1        | 6.99                 | 1.98     | 46  | 53      | 190     |
| 200       | 476.5      | 234.66         | 49.5         | 87.6        | 3.67                 | 1.54     | 59  | 73      | 108     |
| 300       | 448.8      | 201.15         | 79.8         | 72.0        | 1.74                 | 0.99     | 82  | 77      | 92      |

Figure 3. Potentiostatic Polarization curves for uncoated and coated mild steel with 100ppm of FSFD in 1.0 M HCl Solution at 303 K.

Figure 4. Potentiostatic Polarization curves for uncoated and coated mild steel with 200ppm of FSFD in 1.0 M HCl Solution at 303 K.
Figure 5. Potentioatatic Polarization curves for uncoated and coated mild steel with 300ppm of FSFD in 1.0 M HCl Solution at 303 K.

Values of corrosion potentials $E_{corr}$, corrosion current densities $i_{corr}$, cathodic and anodic Tafel slopes $b_c$ and $b_a$. $R_p$ polarization resistance which determination by equation (1), $CR$ corrosion rate determination by equation. (2), the inhibition efficiency of FSFD can calculated from equation (3),

$$R_p = \frac{B}{i_{corr}}$$  \hspace{1cm} (1)

$$R_p = \frac{\beta a \beta c}{2.303 (\beta a + \beta c) i_{corr}}$$

$$CR = 0.13 \left( \frac{e}{p} \right) i_{corr}$$  \hspace{1cm} (2)

e: Chemical equivalent

$p$: density of mild steel

$$I(\%) = \left( \frac{i_{corr} - i_{inh \, corr}}{i_{corr}} \right) \times 100$$  \hspace{1cm} (3)

where $i_{corr}$ and $i_{inh \, corr}$ are referred to the corrosion current density without and with the addition of the inhibitor, respectively.

Result shows that corrosion current density were decreased with increased the concentration of the FSFD compound and the inhibition efficiency increased due to the FSFD effect on the anodic and cathodic the electrochemical corrosion reaction because FSFD contain heteroatoms like nitrogen, sulfur and oxygen atoms as well as lone pairs of electrons present on N, S and O atoms and the planarity are the important structural features that rule to adsorption of these molecules onto the surface of the iron and prevent the continued corrosion [15-16].
3.2 Computational study

3.2.1. Molecular geometry

All the work on the computer was carried out using Gaussian-05 series of programs at the DFT and (B3LYP)/ 6-311G (d, p) basis set level as so to explore the connection among their inhibition efficiency and molecular electronic structure of a new furan derivative (furan-2-ymethyl sulfanyl acetic acid furan-2-ymethylenehydrazide) (FSFD) in ethanol and without solvent (vacuum) as seen in Figure 6. The computational structural parameters such as bond length and dihedral angles were calculated by ChemDraw of Mopac program (ver. 10) as shown in Tables 3 and 4.

![Figure 6. Optimized molecular structure of FSFD compound.](image)

Table 3. Bond length of FSFD compound.

| Bond       | Actual (Å) | Optimal (Å) | Bond       | Actual (Å) | Optimal (Å) |
|------------|------------|-------------|------------|------------|-------------|
| C(1)-O(2)  | 1.3631     | 1.4210      | S(7)-C(8)  | 1.8197     | 1.8150      |
| C(1)-C(5)  | 1.3611     | 1.3370      | C(8)-C(9)  | 1.5230     | 1.5090      |
| C(1)-H(19) | 1.0944     | 1.1000      | C(8)-H(24) | 1.1133     | 1.1130      |
| O(2)-C(3)  | 1.3670     | 1.4210      | C(8)-H(25) | 1.1148     | 1.1130      |
| C(3)-C(4)  | 1.3656     | 1.3370      | C(9)-N(10) | 1.3690     | 1.3673      |
| C(3)-C(6)  | 1.5012     | 1.4970      | C(9)-O(11) | 1.2067     | 1.2080      |
| C(4)-C(5)  | 1.4305     | 1.5030      | N(10)-N(12)| 1.3507     | -           |
| C(4)-H(20) | 1.0962     | 1.1000      | N(10)-H(26)| 1.0096     | 1.0120      |
| C(5)-H(21) | 1.0961     | 1.1000      | N(12)-C(13)| 1.2776     | 1.2600      |
| C(6)-S(7)  | 1.8188     | 1.8150      | C(13)-C(14)| 1.4640     | 1.5030      |
| C(6)-H(22) | 1.1142     | 1.1130      | C(13)-H(27)| 1.1044     | 1.1000      |
| C(6)-H(23) | 1.1135     | 1.1130      |            |            |             |

Table 4. Dihedral angles of FSFD compound.

| Atoms       | Dihedral Angle (deg.) | Atoms       | Dihedral Angle (deg.) |
|-------------|-----------------------|-------------|-----------------------|
| C(1)-O(2)-C(3)-C(6) | 179.049               | H(20)-C(4)-C(5)-H(21) | 0.029                |
| C(1)-O(2)-C(3)-C(4)  | 0.191                 | H(20)-C(4)-C(5)-C(1)  | -179.702             |
| C(6)-C(3)-C(4)-H(20) | 0.814                 | H(23)-C(6)-S(7)-C(8)  | -67.095              |
| C(6)-C(3)-C(4)-C(5)  | -179.049              | H(22)-C(6)-S(7)-C(8)  | 53.027               |
| O(2)-C(3)-C(4)-H(20) | 179.644               | H(24)-C(8)-C(9)-O(11) | 132.787              |
| O(2)-C(3)-C(4)-C(5)  | -0.219                | H(24)-C(8)-C(9)-N(10) | -47.504              |
| C(4)-C(3)-C(6)-H(23) | 148.686               | S(7)-C(8)-C(9)-O(11)  | -103.631             |
| C(4)-C(3)-C(6)-H(22) | 31.787                | S(7)-C(8)-C(9)-N(10)  | 76.076               |
3.2.2 Calculation of the main quantum parameters

The quantum chemical properties such as total energy, energy gap ($\Delta E_{\text{gap}}$), softness ($S$), dipole moment ($\mu$), hardness (η), $E_{\text{HOMO}}$ (highest occupied molecular orbital energy), $E_{\text{LUMO}}$ (lowest unoccupied molecular orbital energy), ionization energy (I), the absolute electronegativity ($\chi$), the fractions of electrons transferred ($\Delta N$), the electrophilicity index (ω), and electron affinity (A) were completed using (DFT) at the (B3LYP) / 6-311G (d, p) basis set as shown in Table 5. Quantum chemical parameters were estimated by using the following equations (1-7):

$$I = -E_{\text{HOMO}}$$  
$$A = -E_{\text{LUMO}}$$  
$$\eta = \frac{I-A}{2}$$  
$$\chi = \frac{I+A}{2}$$  
$$S = \frac{1}{\eta}$$  
$$\Delta N = \frac{X_{Fe}-X_{inh}}{2(\eta_{Fe}+\eta_{inh})}$$  
$$\omega = \frac{\chi^2}{2\eta}$$

Table 5. Quantum chemical parameters for inhibitor FSFD calculated using DFT / B3LYP/ 6-311G (d, p) in ethanol and vacuum solvent.

| Parameters          | Ethanol solvent | Vacuum          |
|---------------------|----------------|----------------|
| total energy (eV)   | -32599.730     | -32599.395     |
| $E_{\text{HOMO}}$ (eV) | -6.286         | -6.122         |
| $E_{\text{LUMO}}$ (eV) | -1.793         | -1.793         |
| $\Delta E_{\text{gap}}$ (eV) | 4.493           | 4.329           |
| $\mu$ (Debye)       | 3.5493         | 2.8168         |
| I (eV)              | 6.286          | 6.122          |
| A (eV)              | 1.793          | 1.793          |
| $\eta$ (eV)        | 2.247          | 2.165          |
| $\omega$ (eV)      | 3.631          | 3.618          |
| $\chi$ (eV)        | 4.0395         | 3.958          |
| S (eV$^{\frac{1}{2}}$) | 0.445          | 0.462          |
| $\Delta N$ (eV)    | 0.658          | 0.703          |

Table 5 shows the theoretical data for FSFD. It is obvious that the values of HOMO energy was increased in ethanol than in vacuum, the HOMO energy is often associated with the electron donating ability of the molecule. So inhibitor with high value of HOMO energy have a tendency to donate electrons to appropriate acceptor with low empty molecular orbital energy. The decrease in the $E_{\text{LUMO}}$ value leads to higher inhibitory efficiency due capability of the FSFD compound to accept electrons from metal iron.

The $\Delta E_{\text{gap}}$ is an important parameter that should be considered. When the energy gap value decreases the reactivity of molecular system increases [17]. Moreover, the $\Delta E_{\text{gap}}$ is a part of the reactivity of the inhibitor molecule towards the adsorption on the metal surface.
As well as, the dipole moment ($\mu$) is the maximum parameter that could be applied to describe the polarity of a molecule [18]. Where an increase in the dipole moment of the molecules leads to an increase in the inhibition efficiency. The inhibitor FSFD has 3.5493 Debye which reflects the increase of the reactivity more than the media without solvent. The electron density distributions, molecular optimization of the frontier molecular orbitals, highest occupied molecular orbital energy and lowest unoccupied molecular orbital energy of the inhibitor FSFD in ethanol solvent and vacuum are presented in Figure (7).

Figure 7. (A) HOMO in ethanol solvent and vacuum and (B) LUMO in ethanol solvent and vacuum of the inhibitor FSFD using DFT / B3LYP / 6-311 G (d, p).

Molecular orbitals HOMO shows that the electronic density is totally centered on the heteroatoms oxygen, nitrogen, sulfur and the furan ring, the LUMO present an important electronic density distributed over most of molecule. This result agrees with the distribution of the Mulliken charges and the direction of the polar direction (moment) are presented in Figure 8 and listed in Table 6.
Figure 8. Mulliken charge distribution (MCD) of the FSFD inhibitor.

Table 6. MCD values (10^{-3}) of the inhibitor FSFD

| Atom | 1C | 2O | 3C | 4C | 5C |
|------|----|----|----|----|----|
| Mulliken charge | 548* | -262 | 131 | -159 | -173 |
| Mulliken charge | 65.6** | -245 | 138 | -145 | -156 |

| Atom | 6C | 7S | 8C | 9C | 10N |
|------|----|----|----|----|-----|
| Mulliken charge | 333 | 668 | -444 | 412 | -274 |
| Mulliken charge | -340 | 118 | -451 | 410 | -280 |

| Atom | 11O | 12N | 13C | 14C | 15O |
|------|-----|-----|-----|-----|-----|
| Mulliken charge | -394 | -182 | 59 | 87 | -259 |
| Mulliken charge | -352 | -159 | 584 | 90 | -251 |

| Atom | 16C | 17C | 18C | 19H | 20H |
|------|-----|-----|-----|-----|-----|
| Mulliken charge | 85 | -174 | -126 | 131 | 116 |
| Mulliken charge | 866 | -162 | 128 | 108 | 971 |

| Atom | 21H | 22H | 23H | 24H | 25H |
|------|-----|-----|-----|-----|-----|
| Mulliken charge | 120 | 177 | 179 | 190 | 184 |
| Mulliken charge | 100 | 153 | 188 | 183 | 168 |

| Atom | 26H | 27H | 28H | 29H | 30H |
|------|-----|-----|-----|-----|-----|
| Mulliken charge | 235 | 148 | 142 | 130 | 130 |
| Mulliken charge | 218 | 136 | 120 | 112 | 117 |

*Ethanol solvent, **Vacuum

Figure 8 and Table 6 display Mulliken charge distribution values. It can be realized that some C atoms and heteroatoms, N, O, S have maximum charge intensity. The large electronic intensity regions are mostly the sites that electrophiles can attack through [19]. Thus, some C atoms, S, O and N are the active cores that easily the atom gives away its electrons to the unoccupied orbital of the metal [20]. Several reports have shown that some heteroatoms with more negatively charged is the more it can be hold as a thin film on the mild steel surface through the donor-acceptor style reaction [21].

4. Conclusions
A new synthesized furan derivative FSFD was investigated using electrochemical measurements and quantum chemical calculations as corrosion inhibition. Experimental results exhibited good corrosion inhibition impact on iron metal surface with maximum inhibition efficiencies of 77% in acidic solution (1.0 M) at 303 K. The contribution of theoretical results has been to confirm with the experimental results.

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