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Experimental and Theoretical Approach to the Corrosion Inhibition of Mild Steel in HCl Solution by a Newly Coumarin †

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Abstract: New coumarin namely 2-(3-(7-methylcoumarin)acetamido)benzoic acid (MAB) was successfully synthesized by reaction of ethyl 2-(7-methylcoumarin)acetate with anthranilic acid. The chemical structure of MAB was confirmed by FT-IR, NMR spectroscopies and Elemental Analysis. The inhibition performance of MAB was investigated using the weight loss method. The results illustrate the strong adsorption of MAB molecules on the mild steel coupon surface and this adsorption follows the Langmuir adsorption isotherm. DFT calculations were performed to show the relationship between the MAP molecular structure and inhibition performance.

Keywords: coumarin 1; corrosion 2; inhibitor 3; anthranilic acid

1. Introduction

As a significant alloy in the universe, mild steel is the substance of choice in oil manufactures for its ability to work mechanical and low coast [1,2]. In most industrial processes, acid is used in the treatment, cleaning and removal of rust [3]. The use of acids during treatment and cleaning processes will lead to corrosion of the metal surface, therefore, an appropriate corrosion inhibitor is urgently needed. Organic compounds containing a heteroatom, such as nitrogen, oxygen, sulfur and phosphorus, or containing double and triple bonds, as well as aromatic rings are considered one of the most important materials recognized in practice and used as anti-corrosion inhibitor. To protect mild steel from corrosive environment, and also to reduce the consumption of acidic solutions that occur during prolonged operation [4–9]. Inhibitors have the ability to control the dissolution of metals and alloys by twisting a layer of anti-corrosion on the surface of the metal or alloy to prevent corrosion thus not exposed to acidic solution [10]. The approach of adsorption inhibitor consists on the inhibitor chemical structure and the nature of the solution acid or base [11]. In general, the cyclic organic compounds containing heteroatoms reported have an excellent inhibition efficiency, but they are limited to use due to the following: (1) high production cost, (2) Toxicity of the secondary compounds which formed during their production or via side reactions resulting in ecological concern and (3) the specificity of work related with the utilize of individual organic corrosion inhibitors. Thus, inhibitors must be active, not expensive and eco-friendly [12,13]. Following up of the investigations for efficient corrosion inhibitor [14–37], this investigation reports the inhibitive effects of new corrosion inhibitor. The synthesized new corrosion inhibitor namely 2-(3-(7-methylcoumarin)acetamido)benzoic acid (MAB), was characterized with FTIR and NMR spectroscopies. The corrosion inhibition behavior on the surface of mild steel in corrosive environment was studied using weight loss techniques. Density functional theory (DFT) were used to corroborate mythological findings.

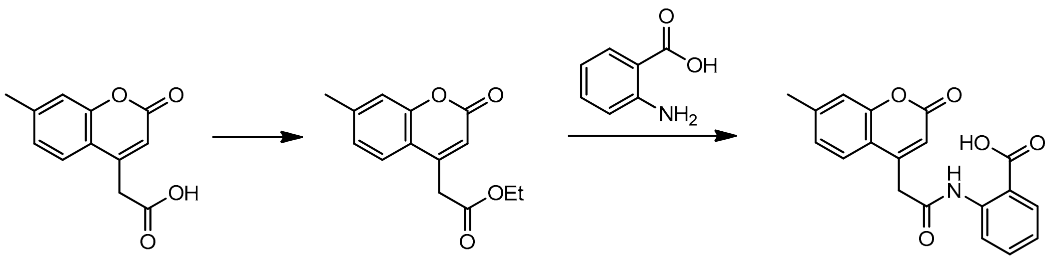
2. Experimental Section

2.1. Materials

Mild steel coupons (2.5 cm × 2.0 cm × 0.025 cm) were used for weight loss techniques with following composition: 99.210Fe; 0.210C; 0.380 Si; 0.090P; 0.05S; 0.050Mn and 0.010Al. The coupons were cleaned with double distilled water, acetone, and dried before each test. The hydrochloric acid solution was used with concentration of 1M as corrosive environment.

2.2. Inhibitor

A mixture of equimolar of methyl 2-(7-methyl-2-oxo-2H-chromen-4-yl)acetate and 2-aminobenzoic acid (2.0 mM) was heated for 24 h at 120 oC. After completion of the reaction, the precipitate was acidified with 2% hydrochloric acid, filtered, recrystallized from ethyl alcohol and dried to yield 55% of yellow solid, melting point: 252 °C. The chemical structure of MAB was demonstrated in Scheme 1. The MAB molecule was characterized by Fourier-transform infrared (FTIR) and Nuclear magnetic resonance (NMR) spectroscopical techniques in addition to a CHN analysis (a carbon, hydrogen and nitrogen analyzer). CHN, analytical calculation/found for the MAB molecule with the chemical formula $C_{19}H_{15}NO_5$: C, 67.65 /67.13; H, 4.48/5.45; N, 4.15/4.07. FT-IR (cm^{-1}): 3283.7 (N-H), 1736.1 (C=O lactone) and 1707.5 (C=O carboxyl). ^{1}H NMR in DMSO-d6 (ppm): δ 2.59 (3H, s), 3.41 (2H, s), 5.89 (1H, s), 7.29-7.41 and 7.61-7.73 (1H, aromatic), 7.88 (1H, NH).



Scheme 1. Chemical structure of the MAB.

2.3.Gravimetric Measurements

The weight loss measurements were performed using mild steel coupons in corrosive environment in absence and presence MAB. The mild steel coupons were cleaned and weighted. Mild steel coupons were immersed in 1 M HCl for 5 h at 303 K in absence and presence MAB. After that the loss in weight was calculated through by the variation in mild steel coupons weights. Corrosion rate (*CR*), inhibition efficiency (*IE*%), and mild steel surface coverage (θ) were measured via Equations (1)–(3).

$$C_R = \frac{W}{At} \tag{1}$$

$$IE\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \tag{2}$$

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \tag{3}$$

where *W* is the loss in weight of the mild steel coupon in milligram, *A* represent the area in cm^2, t is the immersion time in hours and $C_{R(i)}$ is the corrosion rate in presence of MAB.

2.4. DFT

Quantum chemical studies for the molecules of MAB as corrosion inhibitor were performed neutral mode by using of via the Density functional theory calculation with GAUSSIAN 03W software/B3LYP functional [38–40] with a 6–31G basis set [41]. The significant factors have been calculated using the electronic values of the most stable structure of the studied MAB molecules. HOMO and LUMO energies were used to calculate significant parameters such as ΔE, η, σ, χ, and ΔN [42,43] using the following Equations (4)–(7).

$$\Delta E = E_{HOMO} - E_{LUMO} \quad (4)$$

$$\eta = -0.5 \ \ (E_{HOMO} - E_{LUMO}) \quad (5)$$

$$\sigma = \frac{1}{\eta} \quad (6)$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2\eta_{Fe} + 2\eta_{inh}} \quad (7)$$

where χ represent the electronegativity and η represent the represent the hardness.

3. Results and Discussion

3.1. Weight Loss Measurements

The gravimetric results for mild steel coupons in the hydrochloric acid environment with and without of MAB as corrosion inhibitor were demonstrated in Figures 1 and 2.

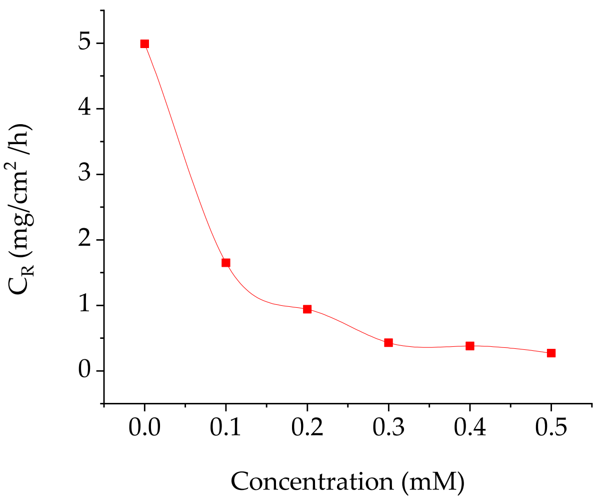


Figure 1. Inhibition efficiencies Corrosion rate for mild steel coupons with and without MAB in 1 M HCl at 308 K.

The excellent inhibition efficiency of new synthesized corrosion inhibitor for mild steel coupons in corrosive environment was attributed to the existence of a number of heteroatoms (Nitrogen and oxygen), aromatic rings and the system α,β-unsaturated carbonyl compound in MAB molecule in addition to big molecular structure of MAB.

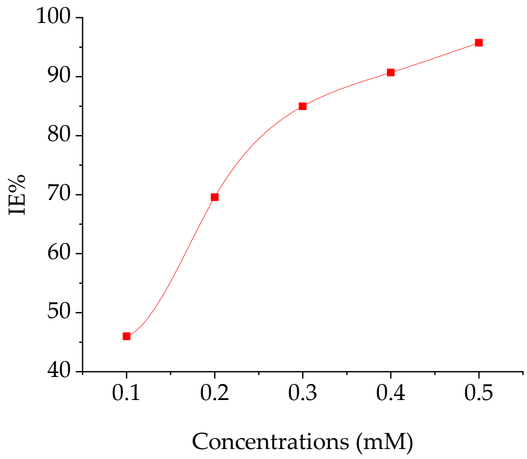


Figure 2. Effect of various concentrations of MAB on the inhibition efficiency for mild steel coupons in 1 M hydrochloric acid at 303 K.

3.2. Adsorption Isotherms

The values obtained for surface coverage (θ) were used by weight loss calculations to find the best and most suitable adsorption isotherm. The adsorption isotherm helps to realize the bonging between the MAP molecules and the coupon surface. The MAP molecules on the coupon surface are absorbed chemically or physically. To realize the adsorption phenomenon, isothermal adsorption (Temkin, Freundlich, and Langmuir isotherms) was utilized to methodological results. It was noted that the adsorption isotherm of Langmuir was very well constructed, with the regression coefficient (R2) value of MAP, indicating a good fit. The obtained slope was 0.78009 and intercept value obtained for the Langmuir isotherm was 2.55971. The Langmuir isotherm plot between C/θ and Ci demonstrate in Figure 3.

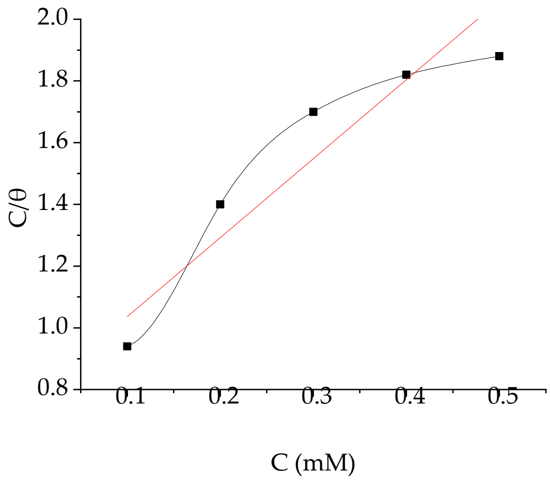


Figure 3. Langmuir adsorption isotherm for mild steel coupon in the presence of MAB.

Adsorption equilibrium constant value was obtained through a straight line of C/θ and C (as in Equation (8)), to obtain free energy of adsorption ΔGads as in Equation (9).

$$\frac{\text{Concentration of the inhibitor } (C)}{Surface\ \ area\ \ (\theta)} = \frac{1}{\text{Adsorption equilibrium } (K_{ads})} + C \quad (8)$$

$$\Delta G_{ads} = -R(\text{gas constant})T(\text{absolute temperature})\ln(55.5K_{ads}) \quad (9)$$

From Equation (9), the ΔGads value was calculated. It is published recently that if ΔGads value in the more negative value of −40 kJ/mol implies chemisorption adsorption. On the other hand if ΔGads value less negative value or around −20 kJ/mol suggest physisorption [44–47]. The ΔGads value for MAB 36.7 kJ/mol, indicates chemisorption adsorption.

3.3. Quantum Chemical Calculations

The DFT studies are quite significant in realizing extra knowledge on the corrosion inhibition phenomenon. The corrosion impedance effectiveness of a molecule as corrosion inhibitor is correlated with some quantum parameters (EHOMO, ELUMO, ΔE, η, σ, χ, and ΔN and Mulliken charges). The quantum studied factors can be observed by the optimization of the investigated inhibitor [48,49].

The quantum chemical factors give the information about the connection between mild steel surface and inhibitor molecules. Herein, the results of this study are demonstrated in Figure 4 and Table 1. The inhibition efficiency of MAB as new synthesized tested corrosion inhibitor can be understanding through HOMO "Highest Occupied Molecular Orbital", and LUMO "Lowest Unoccupied Molecular Orbital". The 3d structure, HOMO and LUMO of MAB are showed in Figure 4. Generally, the value HOMO elucidates the ability of donating electrons of MAB molecule. EHOMO with high value imply that the MAB molecules have a good affinity to donate electrons to an impty orbital of the mild steel surface, whereas the value of LUMO infer to the ability of accepting electrons from mild steel surface. In general, the LUMO with lower value implies that the MAB molecules have the ability to accept electrons from the surface of mild steel coupon through back-donation [50,51].

Hardness and softness are also significant parameters deal with the stability of the inhibitor molecule and reactivity [52].

The hardness with high value and softness with low value infer to a excellent inhibition efficiency [53,54]. Table 1 display that the value ΔE for MAB (7.264 eV) indicate that the MAB is an excellent corrosion inhibitor. The values of ΔE, η, σ and ΔN (fraction of electrons transferred) for MAB are in support of experimental results. The values of EHOMO and ELUMO were −11.628 eV and −4.364 eV respectively, which is agree with the experimental results.

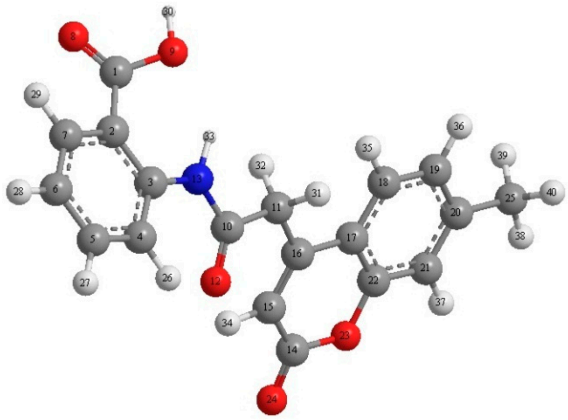
The Mulliken charges were important to figured the adsorption centers of corrosion inhibitor molecules. The atom with high negative charge, has the ability to be adsorbed on the surface of mild steel. From Table 2, the MAB, molecule have the higher negative charges on O8, O9, N12 and O13, which implies that these atoms have the abilities to coordinate with the unoccupied d-orbital of iron atoms on the surface of mild steel.

Table 1. DFT quantum parameters for MAB molecule.

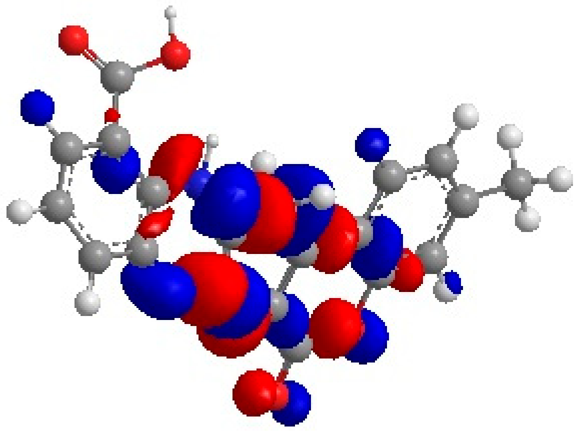
Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE	I	A	σ	χ	η	ΔN
MAB	−11.62	−4.36	−7.26	11.62	4.36	3.632	7.996	0.275	2.539

Table 2. Mulliken Charges of MAB atoms.

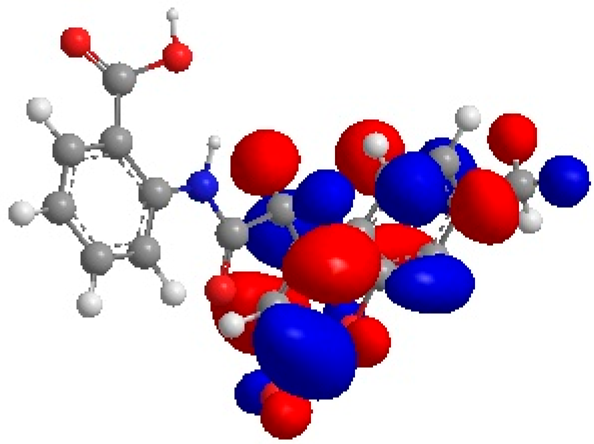
Atoms	Charges	Atoms	Charges	Atoms	Charges	Atoms	Charges	Atoms	Charges
C(1)	0.3580	C(6)	−0.1614	C(11)	−0.1551	C(16)	0.0234	C(21)	−0.1481
C(2)	−0.1526	C(7)	−0.0583	O(12)	−0.3394	C(17)	−0.1421	C(22)	0.1103
C(3)	0.1341	O(8)	−0.3600	N(13)	−0.3396	C(18)	−0.0836	O(23)	−0.1897
C(4)	−0.1593	O(9)	−0.3417	C(14)	0.3312	C(19)	−0.1575	O(24)	−0.2824
C(5)	−0.0739	C(10)	0.3171	C(15)	−0.2074	C(20)	−0.0233	C(25)	−0.1868



(**A**)



(**B**)



(**C**)

Figure 4. Optimized molecular structure (**A**), HOMO (**B**) and LUMO (**C**) of MAB molecule calculated by DFT.

4. Conclusions

1. New coumarin namely 2-(3-(7-methylcoumarin)acetamido)benzoic acid (MAB) was successfully synthesized and the chemical structure of MAB was confirmed by FT-IR, NMR spectroscopies and Elemental Analysis.
2. MAB acts as excellent corrosion inhibitor for mild steel in 1M hydrochloric acid solution.
3. Inhibition performance increased with increasing MAB concentration
4. Evaluation of adsorption isotherm parameters implies the formation of protective layer at the mild steel/corrosive environment interface.
5. Quantum chemical calculations were performed on MAB and various molecular structural factors were estimated and discussed.

Author Contributions: Conceptualization, F.H.; methodology, K.-A.A.; software, S.A.-B.; validation, A.A.-A.; formal analysis, A.A.-A.; investigation, K.A.-A.; resources, F.H.; data curation, S.A.-B.; writing—original draft preparation, A.A.-A.; writing—review and editing, L.S.

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Conflicts of Interest: There are no conflicts to declare.

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