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Research Article

Experimental and Theoretical Studies for Schiff base as best Corrosion inhibitor

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Abstract

In present work, hypothetical and experimental investigations of the corrosion inhibition of mild steel in hydrochloric acid solution utilizing Schiff base namely 2-(4-(dimethylamino)benzylidene)hydrazinecarbothioamide (DH), was done. The inhibition characteristics of DH for the corrosion of mild steel in 1 M hydrochloric acid solution was explored utilizing weight loss strategy. The outcome has demonstrated that the DH is an excellent inhibitor of corrosion of mild steel in HCl. Inhibition efficiencies were 81%, 69% and 36% at 303K, 313K and 323K respectively, that mean the inhibition efficiency of the DH as corrosion inhibitor diminished as temperature expanded and expanded with expansion in concentration. The corrosion inhibition DH was synthesized and it structure was elucidate based on spectroscopic techniques.

Keywords: Corrosion; Mild Steel; Inhibition; hydrazinecarbothioamide.

الخلاصة

البحث الحالي يمثل دراسة نظرية و عملية لمضاد التاكل ضد الفولاذ في حامض الهيدوركلوريك المركز باستخدام قاعدة شف والمسماة 2-(4-(dimethylamino)benzylidene)hydrazinecarbothioamide(DH), ان الخصائص التثبيطية لمركب (DH) كمضاد للتاكل تمت في محلول حمض الهيدروكلوريك (1 مولاري) باستخدام استراتيجية فقدان الوزنوقد اظهرت النتائج ان المركبDH هو مثبط ممتاز لتاكل الفولاذ الطري في محلول حامض الهيدروكلوريك.حيث تبين ان الكفاءة التثبيطية له كانت 36%، 69%، 81% عند درجات حرارة، 323، 313، 303 على التوالي وهذا يعني ان الكفاءة التثبيطية للمركبDH تقلصت عند ارتفاع درجة الحرارة و زيادة التركيز. تم تشخيص المركبات المحضرة باستخدام تقنية الاشعة تحت الحمراء و كذلك تقنية الرنين النووي المغناطيسي.

Introduction

Inhibitors were amongst the most commonsense corrosion protection strategies for shielding metals and amalgams from consumption. Corrosion inhibitors had been broadly considered on mild steel [1]. Mechanism of the corrosion inhibitors could happen by; i-surface adsorption of mild steel and formation of a defensive film; ii- a development of oxide protection film; iii- the reaction between metal and the corrosion inhibitor to form an inorganic complex with coordination bonds [2]. The utilization of corrosive solution in the investigation of corrosion of mild steel had become essential due to the fact that corrosive solutions like H_2SO_4 and HCl are the medium for the most part being utilized for pickling mild steel and mechanical cleaning, and corrosive descaling [3][4]. The protections of mild steel versuscorrosion are noteworthy mechanical issue. The utilization of inhibitors was one of the best choices of ensuring metals against corrosion in corrosive solutions. Most of synthetic inhibitors have heteroatoms and shows corrosion inhibitions [5]. An assessment of corrosion losses demonstrates that the expense of corrosion is enormous. The impact of pipeline corrosion- seepage with the consequent losses, environmental effect, defilement and shutdowns are a portion of the outcomes of corrosion leak. The evaluated of corrosion cost in UK (United Kingdom) and the US (United States) were 13.65$ and 170$ billion in 1969 and 1992 separately. The unfriendly impacts of corrosion could be lessened definitely by comprehension mechanism and subsequent application of corrosion control measures:

infusion of inhibitors compound, protection electrically, pigging operations and integrity evaluation. The utilization of substance inhibitors, for example, rare earth salts, plant extract and synthetic compounds were advantageous and inexpensive [6] [7] [8]. In the present work new corrosion inhibitor has been investigated it inhibition impact on the corrosion of mild steel in hydrochloric acid by weight loss technique. Theoretical studies were used to evaluate some parameters related to the process and were performed using DFT.

Materials and Methods

All chemicals were of analytical reagent grade and were used without further purification. The solutions were prepared by using double distilled water and all experiments were carried out in unstirred solutions. Chemicals were of analytical reagent grade and had been utilized without further process. The solutions were synthesized utilizing distilled water and all investigations were completed without stirred.

Corrosion Inhibitor Preparation

The corrosion inhibitor, namely 2-(4-(dimethylamino) benzylidene) hydrazinecarbothioamide (DH), was synthesized according to the following procedure: refluxing an ethanol solution (100ml) of thiosemicarbazide (0.01 mol) with p-N, N-dimethylaminobenzaldehyde (0.01 mol) for 4 hours, the precipitate formed was collected and recrystallized from ethanol. FT-IR in KBr cm-1; 1617.6 for (C=N); 1222.8 for (C=S). UV-VIS in ethanol 255nm for $\pi \rightarrow \pi^*$ and 338 nm for $n \rightarrow \pi^*$. 1-HNMR 11.48 (s, 1H for NH); 8.26 (s, 2H for NH2) and 8.41(s, 2H for CH=N).

Weight Loss Technique

Weight loss estimations were done by methodology portrayed already [9]. MS specimens with triplicate had been immersed for a time of 2 hours in 100ml of the hydrochloric acid solution both without and with the corrosion inhibitor at the temperatures 303K, 313K and 323K. The average weight loss of the three specimens was utilized toevaluate the inhibition efficiencies utilizing the Equation:

$$IE\% = \frac{w - w^{\circ}}{w} \times 100 \qquad (1)$$

Where w and w^{o} represent the weight losses with and without corrosion inhibitor individually.

Quantum Chemical Calculation

Quantum chemical calculations had been done by DFT (density functional theory) utilizing the level 6-31G (d, p) [10]. The electronic properties such as energy of HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), Eg (energy gap) and other parameters like IP and EA (Ionization potential and Electron affinity) had been evaluated.

Results and Discussion

Preparation of DH

This compound was prepared by the relaxations of p-N, N-di methylaminobenalehyde with thiosemicarbazde in molar ratio 1:1; as shown in Figure 1.

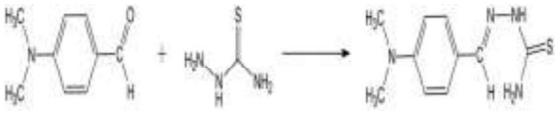

Figure 1: Reaction synthesis of DH inhibitor.

Weight Loss Measurement

Effect of DH concentration

The corrosion inhibition in the absence and presence of various concentrations DH as inhibitor for mild steel in 1M HCl has been studied utilizing weight loss measurements for 2 hours immersion time. Corrosion rate (mpy) as in Figure 1 has been estimated according to the Equations. 2. Where W = weight loss in g, ρ= density of specimen, A = area of specimen and T = time in hours. Where W = weight loss in g, ρ=density of specimen, A = area of specimen and T = time in hours.

$$CR_{(mpy)} = 534 \times W/\rho At \qquad (2)$$

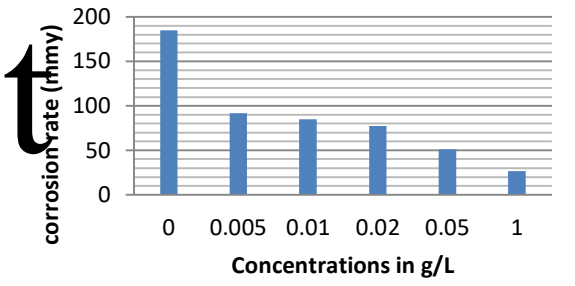

Figure 2: Influences of concentration vs corrosion rate (mmy) for DH inhibitor.

The calculated inhibition efficiencies for mild steel in 1.0M of hydrochloric acid at various concentrations (0, 0.05, 0.1, 0.2, 0.5 and 1.0) (g/L) of the DH (inhibitor) was showed in Figure 2. This conduct can be clarified according to vigorous interactions of the DH molecule with the mild steel surface producing in adsorption [11]. The degree of adsorption increments with the expansion in concentration of the DH prompting expanded inhibition efficiency. In the corrosive solution, the greatest inhibition efficiency had been shown at an DH with concentration of 1.0g/L. Natural and synthetic inhibitors rein the mild steel ending by formalizing a preservative film adsorb to the mild steel surface and isolating it from the corrosion environment [12]. The corrosion inhibitions capacity of the DH molecule begins from the propensity to shape chemically solid bonds with metal utilizing Oxygen and/or nitrogen lone pair of electrons.

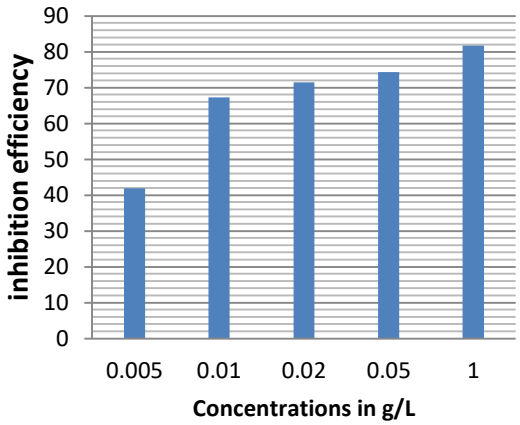

Figure 3: Influences of concentration vs inhibition efficiency for DH inhibitor.

Effect of Temperature

The dissolution behavior of mild steel in 1M hydrochloric acid as a corrosive solution with various concentrations of DH as prepared corrosion inhibitor for 2 hours at range of temperatures such as 303K, 313K and 323K was investigated as clarified in Figure 4. The results showed that DH inhibitor could adsorb on the mil steel surface at all investigated temperatures and corrosion rate (CR) increased with temperature increase in corrosive solution. The inhibition efficiency is decreased with the raise of temperatures as shown in Figure 1.

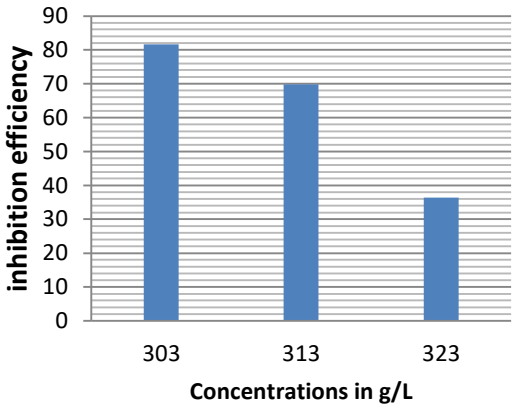

Figure 4: Influences of concentration vs temperature for DH inhibitor.

Quantum Chemical Calculations

Quantum hypothetically computations had been done utilized to explored the collaborations between mild steel and DH (Inhibitor)[13]. HOMO and LUMO of the inhibitor were exhibited in Table 1.

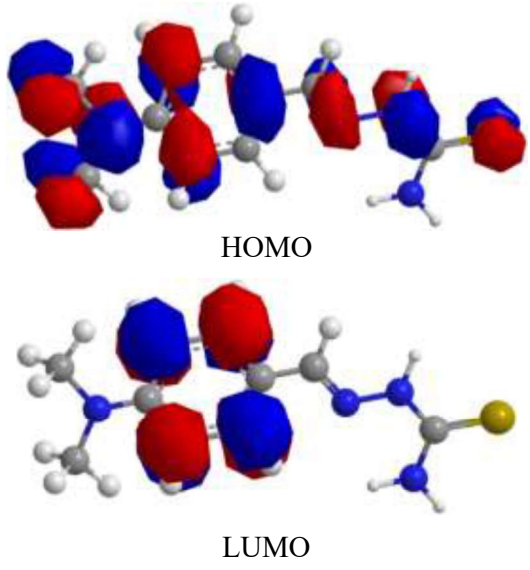

Figure 5: HOMO orbital and LUMO orbitals.

Quantum parameters, like, EHOMO, EHOMO and dipole minute are given in Table 1. The HOMO areas for whole-molecule, that were locales at which electrophile attacks and demonstrate to the dynamic center with the most extreme capacity to cooperate with the mild steel

particles, had donate from nitrogen and/or oxygen. Then again, the LUMO orbital could accepts electrons from the mild steel utilizing anti-bonding orbital form feedback bonds [14].

Table 1: Quantum properties for the Table conformation of DH inhibitor.

HOMO Hartrees	LUMO Hartrees	Band Gap	Dipole moment
-0.27389260 au	-0.03770479 au	-0.23618981	4.135

A high estimation value of the E_{HOMO} shows the inclination of an atom to give electrons to a fitting acceptor particle with unfilled orbitals, while the E_{LUMO} describes the capability of particle toward nucleophilic attacks [15]. Low estimation value of energy-gap suggests that the energy to expel an electron from the orbitals could be minimizing, relating to enhanced inhibition efficiencies [16]. E_{HOMO} as shown in Table 1, do not change essentially for DH inhibitor, which implies that any varieties in the adsorption could be because of molecular-size parameters as opposed to electronic structure parameters. It is obviously, that IE% increments with the highest EHOMO value. The expanding estimations of EHOMO show a higher inclination for the donating electrons to the molecules with a vacant orbital. The heading of corrosion inhibition technique could be prognosticating based on dipole minute (μ). Despite the way that writing is clashing on the use of μ as a marker of the corrosion inhibition interaction, it is generally agreed that the adsorption of polar molecules having higher μ on the mild steel surface should incite better inhibition efficiency. The information got from the investigation demonstrate that the, inhibitor has estimation dipole minute equal to 4.135 and highest IE% is 81 % [17]

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