Quantum mechanical studies of a new inhibitor for the corrosion of mild steel in 2M sulphuric acid

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Abstract

The inhibitive action of 1-cyclohexyl-3-cyclopenta-1,3 dienyl-1,3 diphenyl thiourea (CCDDTU) on corrosion of mild steel in 2M H_2SO_4 has been studied using weight loss, gasometric measurements , potentiodynamic polarization and impedance studies. The studies clearly indicated that inhibitor reduced the dissolution of mild steel in sulphuric acid by behaving as cathodic inhibitor. The adsorption of this organic molecule on mild steel surface obeyed Temkin's adsorption isotherm. The quantum mechanical analysis proved the inhibition efficiency of the compound calculated from chemical and electrochemical measurements.

Keywords : Corrosion inhibitor, Thio compounds, Impedance measurements, Adsorption

Introduction

Mild steel is a main class of materials due to their extensive industrial applications. It is used in many industries due to its excellent mechanical properties. These are employed in industries as pipelines for petroleum industries, storage tanks, acid transporation pumps and valves , shipment vessels and chemical batteries[1] in seashore. Due to their aggresive

nature of sulphate ion , acidic solution will create damage to the steel parts . Numerous methods are used to reduce the corrosion of steel in acidic media. Among them, the use of inhibitors is most commonly adapted [2-3]. Several substituted thioureas have been reported as corrosion inhibitors [4-8] in acidic media. Recently the function of thiourea derivatives as potential corrosion inhibitors for steel in acidic media was studied by Karthikeyan et al [7-8] . The corrosion inhibiting property of these compounds is a structural dependent. The lone pair of electrons decides the adsorption of inhibitor on the metal surface. The present paper describes a study of corrosion protection effect of 1-cyclohexyl-3-cyclopenta-1,3 dienyl-1,3 diphenyl thiourea on corrosion of mild steel in 2M H_2SO_4 using weight loss, gasometric measurements and various electrochemical techniques. Quantum mechanical studies have been performed to validate the role of the inhibitor through adsorption phenomena on steel surface.

But studies on the influence of 1-cyclohexyl-3-cyclopenta-1,3 dienyl-1,3 diphenyl thiourea on hydrogen permeation through mild steel during pickling are very scant. A good inhibitor should have the following two main prerequisites: (1) it should exhibit very good inhibition efficiency and (2) it should lessen the hydrogen permeation current to a considerable extent. Some organic compounds give very high values of inhibition efficiency, but they have a negligible effect in reducing the hydrogen permeation current and vice versa. Compounds which fall under this class are prone to hydrogen embrittlement in a later stage by the combination of permeated atomic hydrogen. This delayed failure creates cracking, pitting, breakage, etc., on the surface of the metal.

As far as we know no concrete report has been published so for CCDDTU in 2M H_2SO_4 with use of potentiodynamic polarization, impedance measurements The structure of the CCDDTU is given in the figure.1. Different concentrations of inhibitor were prepared and their inhibition efficiencies in 2M H_2SO_4 water were investigated.

Experimental methods

Mild steel specimens of compositions, C = 0.08%, P = 0.07%, Si = O%, S = O%, Mn = 0.41% and Fe remainder, and of size 4 x 1 x 0.020 cm were taken for weight loss and gasometric studies. The weight loss study [9] was done at room temperature for two hours in 2M H_2SO_4. The inhibition efficiency (IE %) was determined by the following equation, I.E (%) = $(W_0 - W_i / W_0) \times 100$

Where W_0 & W_i are the weight loss values in the absence and presence of the compound. A mild steel cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of 0.283 cm2 was used for potentiodynamic polarisation and AC impedance measurements.

Both cathodic and anodic polarisation curves were recorded in 2M H_2SO_4potentiodynamically (1 mV s-1) using Sinsil –Electrochemical workstation,USA. A platinum foil and Hg/Hg_2SO_4/2M H_2SO_4 were used as auxiliary and reference electrodes respectively. Double layer capacitance (Cdl) and charge transfer resistance values (R_{ct},) were studied using AC impedance measurements [10-13]. The hydrogen permeation study was carried out using the methodology modified Devanathan and Stachurski's two compartment cell, as reported earlier.[14]. Quantum mechanical calculations were carried using Gaussian software . The energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and dipole moment (μ), were evalaueted with the above given software package.

Results and Discussion

Weight loss and Gasometric measurements

Table 1 gives the results of inhibition efficiency for different concentrations of 1-cyclohexyl-3-cyclopenta-1,3 dienyl-1,3 diphenyl thiourea for the corrosion of mild steel in 2M H_2SO_4 obtained from weight loss and gasometric measurements. It is observed that the inhibitor retards the corrosion of mild steel effectively in salt water. The inhibition of corrosion of brought about by CCDDTU can be due to the following interactions:

1.The interaction between the lone pairs of electrons of the sulfur atom of the inhibitor and the positively charged mild steel surface [10].

2.The affinity of lone pairs of electrons of the nitrogen atoms and the positively charged metal surface [11].

3.The presence of one cyclo hexyl and three benezene moieties in the inhibitor which exerts inductive (+I) effect and increase the electro density on the sulfur atom that leads to effective adsorption of CCDDTU than the unsubstituted thiourea [12] .

A good conformity between the values of inhibition efficiency obtained by weight loss and gasometric methods is found.

Potentiodynamic polarization studies

The corrosion kinetic parameters such as Tafel slopes (b_a and b_c),corrosion current (I_{corr}) and corrosion potential (E_{corr}) and percentage of inhibition measured from tafel plots for mild steel in 2M H_2SO_4 containing different concentrations of inhibitor are presented in table 2.

The values of b_a, b_c and I_{corr} are agreeing well with earlier studies using thiourea derivatives [11-13]. Also, increasing concentrations of CCDDTU enhances the Tafel slopes values,but the values of cathodic Tafel slope b_c are enhanced more. So the inhibition of corrosion of mild steel cathodic control in the present acid media.. Values of E_{corr} are shifted to positive direction in comparision with uninhibited condition in the presence of various concentrations of the inhibitor. This is due to the formation of closely adherent adsorbed film of CCDDTU on the metal surface.

Impedance measurements

Corrosion inhibition of mild steel in 2M H_2SO_4 solution in the presence and absence of inhibitor was monitored by impedance spectroscopy measurements and the results are given in table.3. At all concentrations range of inhbitor , large capacitive loops at higher frequency range followed by small capacitive loops at lower frequency range were visualized [14-18]. Also the values of R_{ct} are found to increase with an increase in concentrations of compound in 2M H_2SO_4 . It was noticed that values of C_{dl} have lessen by increasing concentrations of compound in the acid medium.

Similar results was observed by Harikumar [14] and others [14-18] for the corrosion of mild steel in acidic media using Ampicilin drug and thio compounds as inhibitors.

Hydrogen permeation measurements

Hydrogen permeation measurements results for the dissolution of mild steel in the inhibited and inhibited conditions are presented in Table 4.Hydrogen permeation current for un inhibited mild steel in 2M H_2SO_4 is more, because of the aggressive nature of anions of the acid and also the inhibitor enhances the permeation current . The

enhancement in permeation current can be attributed to the decomposition of the CCDDTU molecules on the steel surface by forming H_2S gas [15-16].. Trabanelli and Zucchi [17] investigated that that sulfur of hydrogen sulfide act as negative catalyst for the recombination of hydrogen atoms into molecular hydrogen. It can be seen from the table that the enhancement of permeation current is more due to the formation of more number of hydrogen sulphide gas , if the concentration of inhibitor is more [18].

Quantum mechanical studies:

The computed quantum chemical parameters like energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), LUMO- HOMO, energy gap (ΔE), dipole moment (μ), are summarized in Table 5. The HOMO and LUMO distribution on thiourea moiety (Figure 3-4) is greater than cyclohexyl moieties and three benzene rings of the compound. According to Tang et al.[20], when a molecule possess similar frontier orbitals, its inhibition efficiency can be correlated to the energy levels of HOMO and LUMO and the difference between them. It has been greatly claimed that, higher the value of E_{HOMO}, greater is the ease for an inhibitor to donate electrons to unoccupied d orbital of metal atom and higher is the inhibition efficiency. Further lower the E_{LUMO}, easier is the acceptance of electrons from metal atom to facilitate good adhesion of inhibitor. The gap between HOMO–LUMO energy levels of molecules was another important parameter that needs to be considered. Higher the value of ΔE of an inhibitor, higher is the inhibition efficiency of that inhibitor. It has been reported that, large values of dipole moment will enhance corrosion inhibition [21-22].

Conclusions

1. 1-cyclohexyl-3-cyclopenta-1,3 dienyl-1,3 diphenyl thiourea inhibits the corrosion of mild steel effectively in high aggressive acid medium.
2. The inhibition of corrosion of mild steel in 2M H_2SO_4 , by the compound is under cathodic control.
3. R_{ct} and C_{dl} values obtained from impedance measurements established the impressive performance of the compound.
4. The adsorption of the compound on mild steel surface follows Temkin's adsorption isotherm.
5. Quantum mechanical studies validate the performance of CCDDTU as excellent corrosion inhibitor for mild steel in 2M H_2SO_4.

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Table 1. Values of inhibition efficiency for the corrosion of mild steel in 2M H_2SO_4 in the presence of different concentrations of CCDDTU obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (ppm)	Inhibition efficiency (%)	
	Weight loss Studies	Gasometric measurements
Blank	---	---
20	72.4	72.6
40	82	81.8
60	90	90.3

Table 2: Corrosion kinetic parameters of mild steel in in 2M H_2SO_4 in the presence of different concentrations of CCDDTU obtained from potentiodynamic polarization studies.

Con. DCHTU	E_{corr} (mV vs SCE)	I_{corr} (µA cm-2)	b_a (mV dec-1)	b_c (mV dec-1)	IE (%)	θ
Blank	-483.12	561.49	86.7	144.1	-	-
20 PPM	-463.38	157.27	75.9	131.9	72.49	0.73
40 PPM	-441.63	104.41	64.1	102.7	82.22	0.82
60 PPM	-431.57	60.15	51.7	91.3	89.8	0.90

Table 3.Impedance values for the corrosion of mild steel in 2M H_2SO_4 in the presence of different concentrations of CCDDTU.

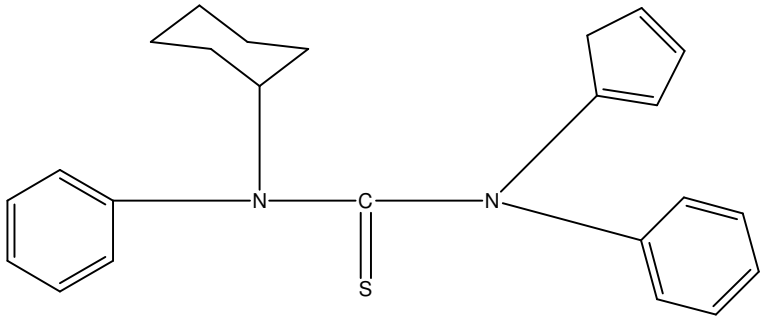
Concentration of Inhibitor (ppm)	Sea water solution	
	Charge Transfer resistance (R_{ct}) Ohm.cm^2	Double layer capacitance (C_{dl}) µF.cm^{-2}
Blank	51	169
20	123	64
40	164	43
60	187	18

Table 4. Values of permeation current for the corrosion of mild steel in 2M sulphuric acid in the presence of different concentrations of inhibitor .

Concentration of Inhibitor (ppm)	**Steady state permeation current (µA)**
	2M H_2SO_4
Blank	34.7
20	38.5
40	44.2
60	48.3

Table 5: Quantum mechanical parameters for the inhibitor

Compound	**LUMO (eV)**	**HOMO (eV)**	**ΔE (Cal.Mol^{-1})**	**Dipole moment (Debye)**
Cyclohexyl thiourea	-0.04018	-4.73957	4.77975	2.5453



1-cyclohexyl-3-(cyclopenta-1,3-dienyl)-1,3-diphenylthiourea

Figure 1 Structure of inhibitor

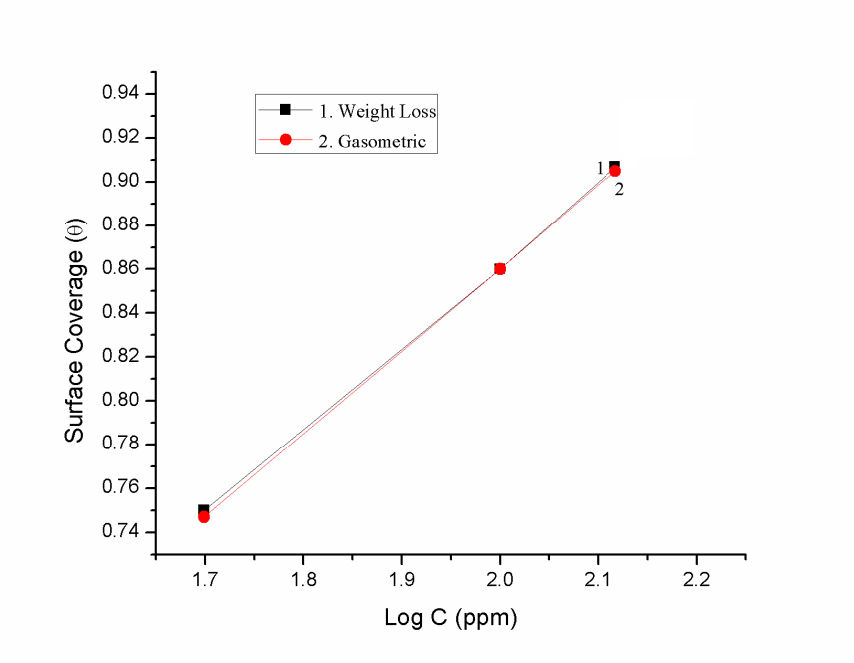


Figure 2 Temkin's adsorption isotherm for CCDDTU in 2M H_2SO_4.

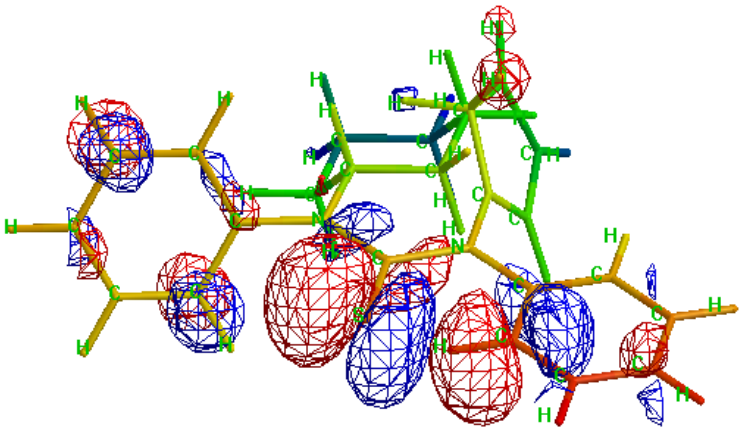


Figure 3. Highly occupied molecular orbital (HOMO) for CCDDTU.

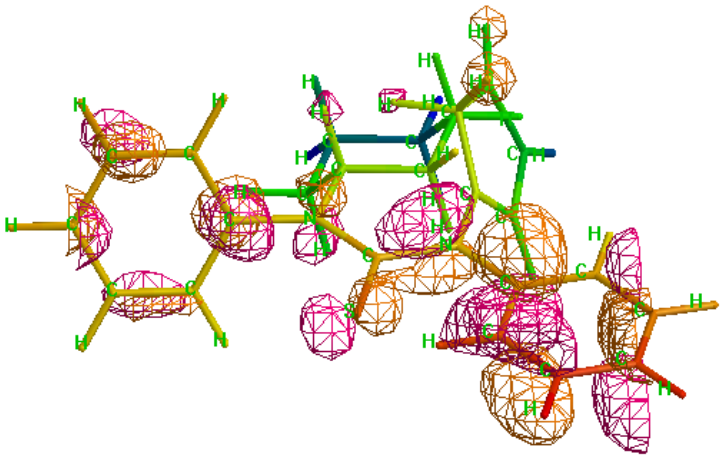


Figure 4. Lowest unoccupied molecular orbital (LUMO) for CCDDTU.