



## DICYCLOHEXYL THIOUREA AS AN INHIBITOR FOR THE CORROSION OF MILD STEEL IN SALT WATER

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### ABSTRACT

The inhibitive action of dicyclohexyl thiourea (DCHTU) on corrosion of mild steel in 3.5% NaCl (3.5% NaCl) has been studied using weight loss, gasometric measurements, potentiodynamic polarization and impedance studies. The studies clearly indicated that DCHTU acted as cathodic inhibitor. The adsorption of the compound on mild steel surface obeyed Temkin's adsorption isotherm. Diffused reflectance spectra and SEM images confirmed the formation of adsorbed film of inhibitor on metal. The quantum chemical analysis substantiates the inhibition efficiency of the compound determined by electrochemical methods.

**Key words:** Corrosion inhibitor, Thio compounds, Impedance measurements, Adsorption.

### INTRODUCTION

Mild steel is an important category of materials due to their wide range of industrial applications. It is used in many industries due to its excellent mechanical properties. These are used in industries as pipelines for petroleum industries, storage tanks, shipment vessels and chemical batteries<sup>1</sup> in seashore. Due to their high corrosive nature, salt water may cause damage to the steel components. Various methods are used to decrease the corrosion of steel in salt water. Among them, the use of inhibitors is most commonly suggested<sup>2-3</sup>. Several substituted thioureas have been investigated as corrosion inhibitors<sup>4</sup>. Most of the effective organic inhibitors have heteroatom such as O, N, S containing multiple bonds in their molecules through, which they can adsorb on the metal surface<sup>2-6</sup>. Recently thiourea derivatives have been reported as an excellent corrosion inhibitor in acidic media by

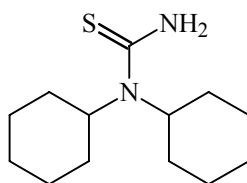
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Karthikeyan et al.<sup>7-8</sup> The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair of electrons determines the adsorption of these molecules on the metal surface. The present paper describes a study of corrosion protection action of dicyclohexyl thiourea on corrosion of mild steel in 3.5% NaCl using weight loss, gasometric measurements and various electrochemical techniques. Quantum mechanical studies have been carried out to substantiate the inhibition performance of the compound through mere adsorption on steel surface.

But studies on the influence of dicyclohexyl thiourea on hydrogen permeation through steel substrate during pickling are very scarce. A good inhibitor should have the following two important requisites: (1) it should have very good inhibition efficiency and (2) it should bring down 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 come under this class produce hydrogen embrittlement in a later stage by the combination of permeated atomic hydrogen. This delayed failure creates cracking, pitting, breakage, etc, on the metal surface.

Dicyclohexyl thiourea is an organic compound with  $\pi$ -electrons and heteroatom's S, N and O. The molecule is big enough (Melting point : 135°C) and sufficiently planar to block more surface area due to adsorption on mild steel. These factors favour the interaction of DCHTU with the metal. As far as we know no concrete report has been published so far for DCHTU in 3.5% NaCl with use of potentiodynamic polarization, impedance measurements and diffuse reflectance spectra. The structure of the DCHTU is shown in the Fig. 1. Different concentrations of inhibitor were prepared and their inhibition efficiencies in 5% salt water were investigated.



**Fig. 1: Structure of dicyclohexyl thiourea**

## EXPERIMENTAL

Mild steel specimens of compositions, C = 0.08%, P = 0.07%, Si = 0%, S = 0%, Mn = 0.41% and Fe remainder, and of size 4 x 1 x 0.020 cm were used for weight loss and gasometric studies. The weight loss study was carried out at room temperature for three

hours in 3.5% NaCl. The inhibition efficiency (IE %) was determined by the following equation,  $IE (\%) = (W_0 - W_i / W_0) \times 100$ .

Where  $W_0$  and  $W_i$  are the weight loss values in the absence and presence of the inhibitor. A mild steel cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of  $0.283 \text{ cm}^2$  was used for potentiodynamic polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier<sup>9</sup>. Both cathodic and anodic polarisation curves were recorded in 3.5% NaCl potentiodynamically ( $1 \text{ mA s}^{-1}$ ) using corrosion measurement system BAS Model: 100A computerised electrochemical analyzer (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil and Hg/Hg<sub>2</sub>Cl<sub>2</sub>/ 5% NaCl were used as auxiliary and reference electrodes, respectively. Double layer capacitance (Cdl) and charge transfer resistance values ( $R_{ct}$ ) were measured using AC impedance measurements<sup>10-13</sup>. The hydrogen permeation study was carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell, as described earlier<sup>14</sup>. The surfaces of corroded and corrosion inhibited mild steel specimens were examined by diffuse reflectance studies in the region 200-700 nm using U-3400 spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan). Quantum mechanical calculations were carried using MOPAC 2000 program of CS Chemoffice packet program. The energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and dipole moment ( $\mu$ ), were calculated with the above given software package.

## RESULTS AND DISCUSSION

### Weight loss and gasometric measurements

Table 1 gives the values of inhibition efficiency for different concentrations of dicyclohexyl thiourea for the corrosion of mild steel in 3.5% NaCl obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of mild steel effectively in salt water. The inhibition of corrosion of brought about by dicyclohexyl thiourea can be due to the following interactions:

1. The interaction between the lone pairs of electrons of the sulfur atom of the organic molecule and the positively charged metal surface<sup>10</sup>.
2. The interactions between lone pairs of electrons of the nitrogen atoms and the positively charged metal surface<sup>11</sup>.

- The presence of two cyclohexyl groups in the molecule, which shows inductive (+ I) effect may increase the electro density on the sulfur atom that leads to better performance than the unsubstituted thiourea<sup>12</sup>.

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

**Table 1: Values of inhibition efficiency for the corrosion of mild steel in 3.5% NaCl in the presence of different concentrations of dicyclohexyl thiourea obtained from weight loss and gasometric measurements**

Concentration of inhibitor (ppm)	Inhibition efficiency (%)	
	Weight loss studies	Gasometric measurements
Blank	-	-
25	73	72.6
50	82	82
75	90	90.3

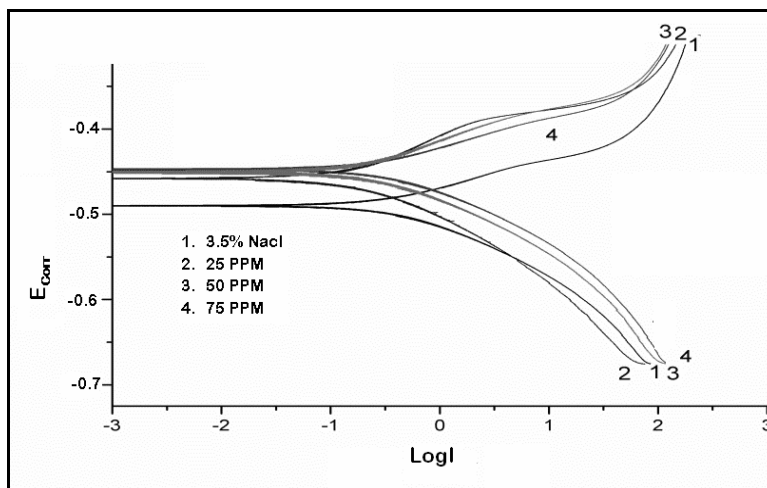
#### Potentiodynamic polarization studies

The corrosion kinetic parameters such as Tafel slopes ( $b_a$  and  $b_c$ ), corrosion current ( $I_{corr}$ ) and corrosion potential ( $E_{corr}$ ) and inhibition efficiency obtained from potentiodynamic polarization curves for mild steel in 3.5% NaCl containing different concentrations of inhibitor are given in Table 2.

**Table 2: Corrosion kinetic parameters of mild steel in 3.5% NaCl in the presence of different concentrations of DCHTU obtained from potentiodynamic polarization studies**

Con. $\theta$ DCHTU	$E_{corr}$ (mV vs SCE)	$I_{corr}$ ( $\mu\text{A cm}^{-2}$ )	$b_a$ (mV dec <sup>-1</sup> )	$b_c$ (mV dec <sup>-1</sup> )	IE (%)
Blank	-489.32560.57	87.0	145.3	-	-
25 PPM	-466.18155.37	76.2	132.0	72.28	0.72
50 PPM	-440.82104.67	64.4	103.2	81.30	0.81
75 PPM	-432.1860.45	51.4	92.0	89.2	0.89

The values of  $b_a$ ,  $b_c$  and  $I_{\text{corr}}$  are very much similar to those reported earlier<sup>11,12</sup>. Further it is ascertained that increasing concentrations of DCHTU enhances the values of both  $b_a$  and  $b_c$ , but the values of  $b_c$  are enhanced to greater a extent. So the inhibition of corrosion of mild steel in salt water is under cathodic control. Values of  $E_{\text{corr}}$  is shifted to less negative values in the presence of different concentrations of compound. This can be ascribed to the formation of closely adherent adsorbed film on the metal surface. The results of potentiodynamic polarization for the corrosion of mild steel in 3.5% NaCl are given in Fig. 2.

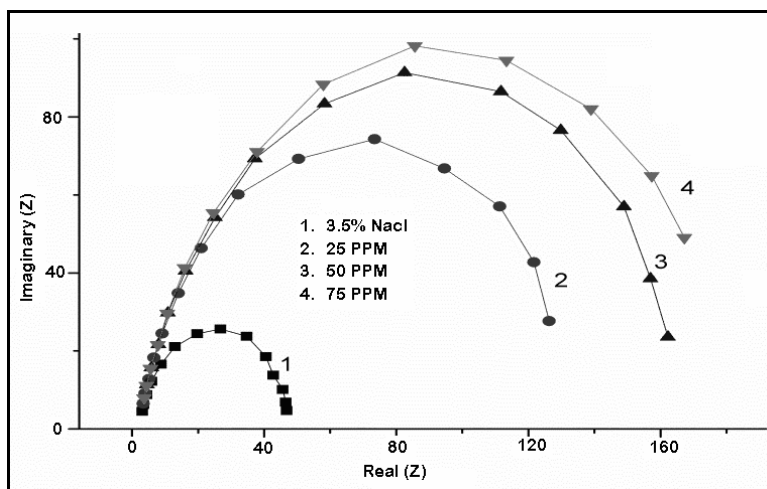


**Fig. 2: Potentiodynamic polarization plot for mild steel in 3.5% NaCl with different concentrations of inhibitor**

### Impedance measurements

Corrosion inhibition of mild steel in 3.5% NaCl solution with and without inhibitor was investigated by electrochemical impedance spectroscopy measurements and it is shown in Fig. 3 and the results are presented in Table 3. At all concentrations range of DCHTU, large capacitive circle at higher frequency range followed by small capacitive loops at lower frequency range. The diameter of the circles increased with the increase in inhibitor concentration. The higher frequency capacitive loop is due to the adsorption of inhibitor molecule<sup>13-17</sup>. Also the values of  $R_{\text{ct}}$  are found to increase with an increase in concentrations of compound in 3.5% NaCl solution. It is found that values of  $C_{\text{dl}}$  are fetched down by increasing concentrations of inhibitors in the acid. This can be ascribed to the well-built adsorption of the compounds on the metal surface.

Similar observation was reported by Harikumar<sup>14</sup> and others<sup>13-17</sup> for the corrosion inhibition of mild steel in acidic media by Ampicilin drug and thio compounds.



**Fig. 3: Impedance curves for the corrosion of mild steel in 3.5% NaCl in the presence and absence of DCHTU**

**Table 3: Impedance values for the corrosion of mild steel in 3.5% NaCl in the presence of different concentrations of dicyclohexyl thiourea**

Concentration of inhibitor (ppm)	Sea water solution	
	Charge transfer resistance ( $R_{ct}$ ) Ohm.cm <sup>2</sup>	Double layer capacitance ( $C_{dl}$ ) $\mu$ F.cm <sup>-2</sup>
Blank	47	165
25	130	68
50	167	46
75	182	21

### Hydrogen permeation measurements

Hydrogen permeation measurements results for the corrosion of mild steel in the presence and absence of the inhibitor are presented in Table 4. Hydrogen permeation current for mild steel in 3.5% NaCl is more, because of the aggressive nature of chloride ions. It can be seen from the table that dicyclohexyl thiourea enhances the permeation current. The enhancement in permeation current can be attributed to the decomposition of the compound

on the mild steel surface<sup>13</sup>. In all the mechanisms suggested so far, invariable the product of decomposition of dicyclohexyl thiourea is H<sub>2</sub>S, which is evolved on the metal surface. Its formation can be detected by radiometric measurements, if labeled thiourea or its derivatives are used<sup>7,8,14</sup>. The whole process takes place in two stages. In the first stage, cyclohexyl thiourea molecules are adsorbed on the metal surface by virtue of the interaction of lone pairs of electrons of nitrogen and sulfur. In the second stage, the adsorbed molecules of the compound slowly undergo chemical changes. The molecule usually decomposes with the formation of H<sub>2</sub>S by the action of hydrogen evolved on the metal.

Hough et al.,<sup>16</sup> investigated that the enhanced permeation of hydrogen ions through the metal surface in acidic solutions in the presence of thiourea and derivatives may be due to the presence of increased concentration of surface hydrogen atoms. This can be attributed to the inhibition of the recombination of hydrogen atoms to form hydrogen molecules. Trabanelli and Zucchi<sup>17</sup> reported that sulfur of hydrogen sulfide can act as a 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, if the concentration of dicyclohexyl thiourea is more. A similar observation has been made by Lahiri et al.,<sup>18</sup> that hydrogen permeation current increases with increase in the concentration of di-ortho tolyl thiourea.

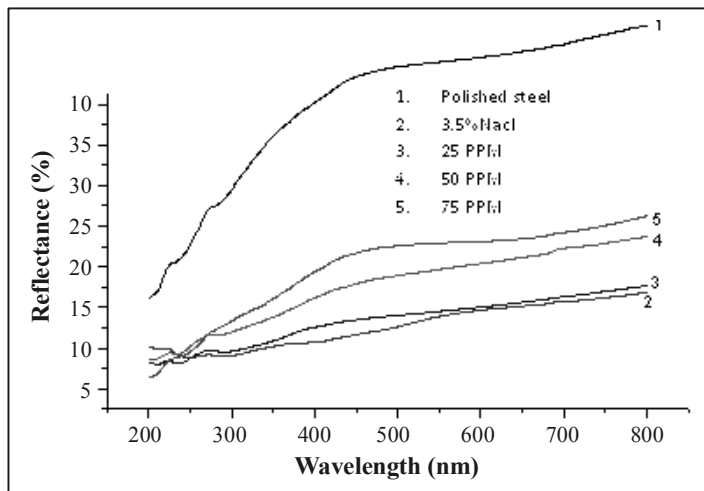
**Table 4: Values of permeation current for the corrosion of mild steel in 3.5% NaCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of cyclohexyl thiourea**

Concentration of Inhibitor (mM)	Steady state permeation current (μA)
	3.5% NaCl
Blank	24
25	28.4
50	34.4
75	38.3

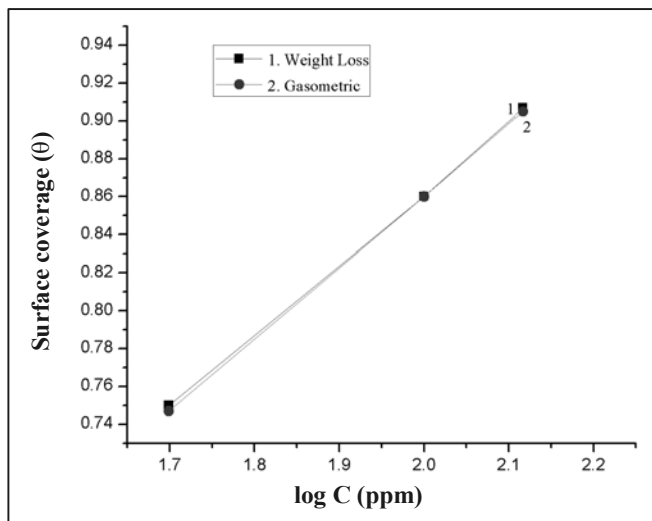
#### Diffused reflectance studies

The formation of thin film on the surface of mild steel is ascertained by UV reflectance studies carried out using a spectrophotometer in different concentrations of inhibitor with different mild steel specimens. The reflectance curves for polished specimen, specimen dipped in salt water and different concentrations of inhibitor are shown in Fig. 4. The percentage of reflectance is maximum for polished mild steel and it gradually decreases for

the specimen dipped in 3.5% NaCl solution. This observation reveals that the change in surface characteristic is due to the corrosion of mild steel in salt water. When compared with uninhibited solution, the reflectance percentage increased as the concentration of the inhibitor increased. This can be ascribed to the increase in film thickness formed on mild steel surface<sup>19</sup>. The plot of  $\log C$  vs  $\theta$  (Fig. 5) gives a straight line indicating that the adsorption of this compound on steel surface follows Temkin's adsorption isotherm.



**Fig. 4: UV Reflectance curves for mild steel in salt water with different concentrations of inhibitor**



**Fig. 5: Temkin's adsorption isotherm for DCHTU in 3.5% NaCl water.**

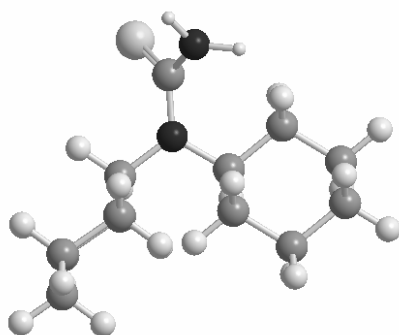


### Quantum mechanical studies

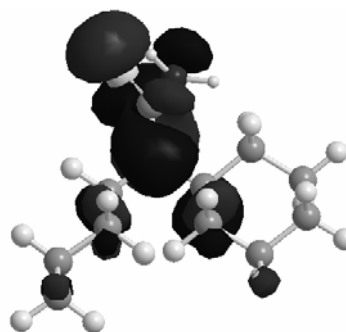
The computed quantum chemical parameters like energy of highest occupied molecular orbital ( $E_{\text{HOMO}}$ ), energy of lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), LUMO-HOMO, energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), are summarized in Table 5. The HOMO and LUMO distribution on thiourea moiety (Fig. 6-8) is greater than cyclohexyl moieties of the compound.

**Table 5: Quantum mechanical parameters for the inhibitor**

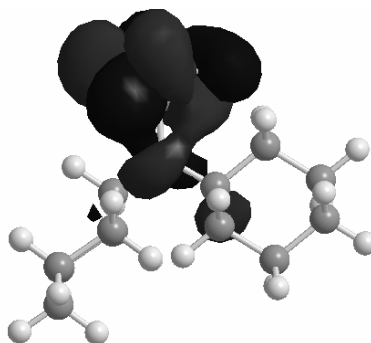
Compound	LUMO (eV)	HOMO (eV)	$\Delta E$ (Cal.mol <sup>-1</sup> )	Dipole moment (Debye)
Cyclohexyl thiourea	0.197018	-8.13957	8.336588	4.5453



**Fig. 6: Optimized structure of DHTU**



**Fig. 7: Highly occupied molecular orbital (HOMO) for DHTU**



**Fig. 8: Lowest unoccupied molecular orbital (LUMO) for DHTU**

According to Tang et al.<sup>21</sup>, 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  $E_{\text{HOMO}}$ , 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  $E_{\text{LUMO}}$ , easier is the acceptance of electrons from metal atom to form feedback bonds. The gap between HOMO–LUMO energy levels of molecules was another important parameter that needs to be considered. Higher the value of  $\Delta E$  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<sup>21,22</sup>.

## CONCLUSION

- (i) Dicyclohexyl thiourea inhibits the corrosion of mild steel effectively in 3.5% NaCl.
- (ii) The inhibition of corrosion of mild steel in salt water, by the compound is under cathodic control.
- (iii)  $R_{\text{ct}}$  and  $C_{\text{dl}}$  values obtained from impedance measurements confirm the better performance of the compound.
- (iv) The adsorption of the compound on mild steel surface obeys Temkin's adsorption isotherm.
- (v) UV-reflectance studies reveal the mere adsorption of the inhibitor on the mild steel surface accounted for the corrosion inhibition of steel in 3.5% NaCl.
- (vi) The presence of inhibitor in 3.5% NaCl is found to enhance the ingress of hydrogen through mild steel.
- (vii) The quantum mechanical studies substantiate the performance of DHTU as excellent corrosion inhibitor for mild steel in salt water.

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