

# The inhibitive action of Cyclohexyl thiourea on the corrosion and hydrogen permeation through mild steel in acidic solutions

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**Abstract:** The influence of Cyclohexyl thiourea (CHTU) on corrosion and hydrogen permeation through mild steel in 1N H<sub>2</sub>SO<sub>4</sub> and 1N HCl has been studied using weight loss measurements and various electrochemical techniques. The compound is found to be more inhibitive in H<sub>2</sub>SO<sub>4</sub> than in HCl. Potentiodynamic polarization studies clearly indicate that CHU behaves as a cathodic inhibitor. Hydrogen permeation studies and AC impedance measurements also prove an improved performance of the compound in H<sub>2</sub>SO<sub>4</sub>. The adsorption of this compound on the mild steel surface obeys Temkin's adsorption isotherm.

**Keywords :** Corrosion inhibitor, Cyclohexyl thiourea, hydrogen permeation.

## Introduction

Thiourea and its derivatives have been studied for more than four decades because they inhibit the corrosion of steels and are superior to amine-based inhibitors in acid media[1-3]. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are potential corrosion inhibitors. While extensive investigations have been carried out on inhibitor

properties of thiourea, due attention has not yet been paid to a systematic study of inhibitor action of thiourea derivatives. However, several substituted thiourea have been investigated as corrosion inhibitors<sup>4</sup>. Most of the effective organic inhibitors have heteroatoms such as O, N, S containing multiple bonds in their molecules through which they can adsorb on the metal surface[5-8]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair determines the adsorption of these molecules on the metal surface. All the above studies reveal the one

common observation that thiourea derivatives can be regarded as excellent corrosion inhibitors. But studies on the influence of cyclohexyl 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.

### **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 hydrogen permeation studies. A mild steel cylindrical rod of the same composition as above and embedded in araldite resin

with an exposed area of 0.283 cm<sup>2</sup> was used for galvanostatic polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier. [9] Both cathodic and anodic polarisation curves were recorded potentiodynamically (1 mA s<sup>-1</sup>) using corrosion measurement system BAS Model: 100A computerised electrochemical analyser (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil, Hg/Hg<sub>2</sub>Cl<sub>2</sub>/1 N HCl and Hg/HgSO<sub>4</sub>/1 N H<sub>2</sub>SO<sub>4</sub> were used as auxiliary and reference electrodes, respectively. The hydrogen permeation study was carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell, as described earlier.[4] Double layer capacitance (C<sub>dl</sub>) and charge transfer resistance values (R<sub>c</sub>) were obtained using AC impedance measurements as described in an earlier publication." 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).

**Table 1. Values of inhibition efficiency for the corrosion of mild steel in 1M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of Cyclohexyl thiourea obtained from weight loss and gasometric measurements.**

Concentration of Inhibitor (mM)	Inhibition efficiency (%)				
	HCl		H <sub>2</sub> SO <sub>4</sub>		
	Weight loss Studies	Gasometric measurements	Weight loss studies	Gasometric measurements	Gasometric measurements
1	80	80.4	91.2	91.8	91.8
5	84.2	84.7	94.3	95.2	95.2
10	90.0	90.4	95.7	96.4	96.4
50	94.4	94.7	97.2	97.9	97.9
100	97.4	97.9	99.2	99.6	99.6

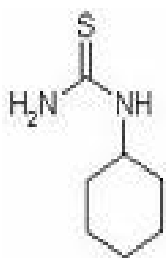
### **Results and Discussion**

#### **Weight loss and Gasometric measurements**

Table 1 gives the values of inhibition efficiency for different concentrations of cyclohexyl thiourea for the corrosion of mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of mild steel in both acids, but more effectively in H<sub>2</sub>SO<sub>4</sub>. This can be attributed to the lesser adsorption of sulphate ions

on the metal surface, thereby leaving more space for the organic molecules to get adsorbed. But in the of HCl the stronger adsorption of the chloride ions on the metal surface leaves less space for organic molecules to get adsorbed. So in H<sub>2</sub>SO<sub>4</sub>, the coverage of the metal surface by the organic molecules is significantly more, giving rise to higher values of inhibition efficiency for all concentrations of the compound used<sup>9</sup>.

The structure of the compound is given in Figure 1.



**Figure 1. Structure of Cyclohexyl thiourea.**

The inhibition of corrosion of brought about by Cyclohexyl 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[10].

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

3.The presence of cyclohexyl group 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[12].

It is found that there is very good conformity between the values of inhibition efficiency obtained by weight loss and gasometric methods.

### **Potentiodynamic polarization studies**

**Table 2(a) and 2(b) give** values of 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 1M HCl and 0.5 M  $H_2SO_4$  containing different concentrations of inhibitor. It can be seen from this table that values of Tafel slopes and  $I_{corr}$  are very much similar to those reported earlier[12,13]. Further it is ascertained that increasing concentrations of Cyclohexyl thiourea enhances the values of both  $b_a$  and  $b_c$ , but the values of  $b_c$  are enhanced to greater extent. So the inhibition of corrosion of mild steel in both acids is under cathodic control. Values of  $E_{corr}$  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 presence of increasing concentrations of cyclohexyl thiourea retards  $I_{corr}$  values in both the acids. It can also be seen that most of the values of inhibition efficiency obtained by weight loss measurements and potentiodynamic polarization studies agree very well.

**Table 2.a Corrosion kinetic parameters of mild steel in 1M HCl in the presence of different concentrations of Cyclohexyl thiourea obtained from potentiodynamic polarization studies.**

Concentration of Inhibitor (mM)	$E_{corr}$ (mV)	Tafel slopes in mV in $dec^{-1}$		$I_{corr}$ $mA\ cm^{-1}$	Inhibition efficiency (%)
		$b_a$	$b_c$		
Blank	-510	66	119	2.79	---
1	-495	74	128	0.43	84.5
10	-483	75	135	0.30	89.2
50	-477	78	139	0.16	94.2
100	-471	84	144	0.09	96.7

**Table 2.b Corrosion kinetic parameters of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of Cyclohexyl thiourea obtained from galvanostatic polarization studies.**

Concentration of Inhibitor (mM)	E <sub>corr</sub> (mV)	Tafel slopes in mV in dec <sup>-1</sup>		I <sub>corr</sub> mA cm <sup>-1</sup>	Inhibition efficiency (%)
		b <sub>a</sub>	b <sub>c</sub>		
Blank	-909	70	130	2.25	---
1	-889	70	137	0.20	91.0
10	-880	76	137	0.14	93.6
50	-874	79	139	0.07	96.7
100	-868	80	149	0.03	98.5

**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 3. Hydrogen permeation current for mild steel in 1N HCl is more, because of the aggressive nature of chloride ions. It can be seen from the table that the presence of Cyclohexyl thiourea in both acids enhances the permeation current. The enhancement in permeation current can be attributed to the decomposition of the compound on the mild steel surface[14]. In all the mechanisms suggested so far, invariable the product of decomposition of cyclohexyl 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 35 s or its derivatives are used[15]. 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 sulfur. In the second stage, the adsorbed molecules of the compound slowly undergoes 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[16] 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[17] reported that sulfur of hydrogen sulfide can 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, if the concentration of cyclohexyl thiourea is more. A similar observation has been made by Lahiri et al[18] that hydrogen permeation current increases with increase in the concentration of di-ortho tolyl thiourea.

**Impedance studies**

Values of charge transfer resistance (R<sub>t</sub>) and double layer capacitance (C<sub>dl</sub>) derived from Nyquist plots are shown in table 4. It can be seen in table that the values of R<sub>t</sub> is found to increase with increase in concentration of compound in both the acids. Values of double layer capacitance are found to be more for 1N HCl than for 1N H<sub>2</sub>SO<sub>4</sub>. It is found that values of C<sub>dl</sub> are brought down by increasing concentrations of inhibitor in both the acids. This can be attributed to increasing adsorption of the compound on the metal surface with increase in its concentration.

A plot of surface coverage (θ) versus log C gives a straight line showing that the adsorption of CHTU on the mild steel surface from both acids obeys Temkin's adsorption isotherm. This points to corrosion inhibition by this compound, being a result of its adsorption on the metal surface.

**Table 3. Values of permeation current for the corrosion of mild steel in 1M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of Cyclohexyl thiourea.**

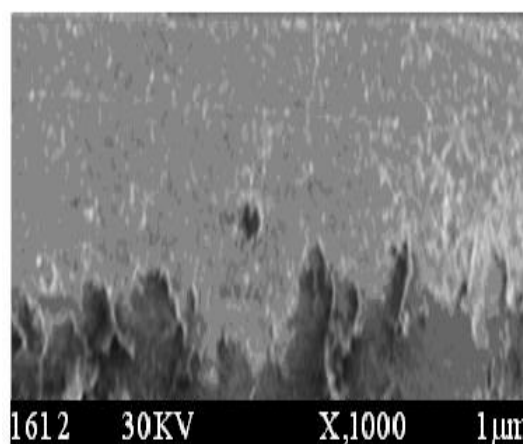
Concentration of Inhibitor (mM)	Steady state permeation current ( $\mu\text{A}$ )	
	1M HCl	1M H <sub>2</sub> SO <sub>4</sub>
Blank	22.7	12.7
1	25.6	12.8
10	23.5	13.7
50	24.0	14.4
100	24.8	15.9

**Table 4. Impedance parameters for the corrosion of mild steel in 1M HCl 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)	HCl		H <sub>2</sub> SO <sub>4</sub>	
	Charge Transfer resistance ( $R_t$ ) Ohm.cm <sup>2</sup>	Double layer capacitance ( $C_{dl}$ ) $\mu\text{F.cm}^{-2}$	Charge Transfer resistance ( $R_t$ ) Ohm.cm <sup>2</sup>	Double layer capacitance ( $C_{dl}$ ) $\mu\text{F.cm}^{-2}$
Blank	4.5	245	6.8	187
1	30	170	31	172
10	42.3	135.2	44	133
50	70.5	120	78.4	109.2
100	88.3	100	90.5	98.2

**SEM**

SEM photographs obtained for mild steel surface immersed in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> solutions for 3 hrs in the absence and presence of 100 mM of CHTU are shown in Fig 2 (a, b, c & d). It can be observed from Fig 2a & Fig 2b, that the specimen surfaces were strongly damaged in the absence of the inhibitor. SEM image of inhibited mild steel specimen (Fig. 2c & 2 d) reveals that a good protective adsorbed film is formed on the specimens surface, which suppresses the rate of corrosion, being responsible for the inhibition.

**Figure 2.a .SEM PHOTOS OF MILD STEEL 1N HCL**

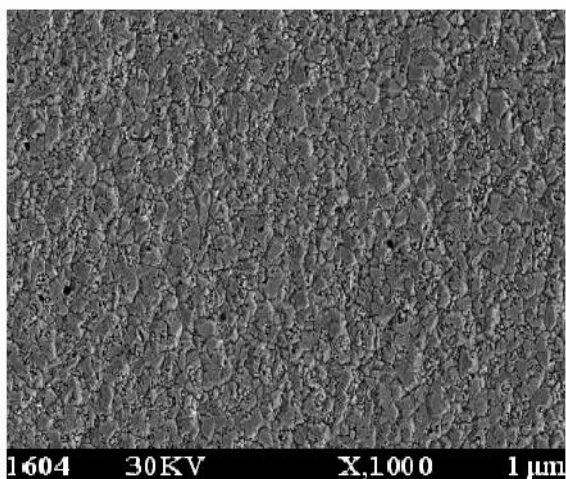


Figure 2.b .SEM PHOTOS OF MILS STEEL IN 1 M H<sub>2</sub>SO<sub>4</sub>

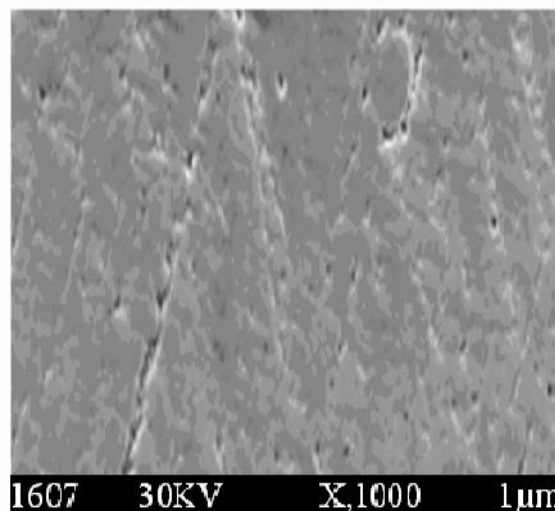


Figure 2.c SEM PHOTOS OF MILD STEEL IN THE PRESENCE OF CHTU (100 ppm) IN 1N HCL

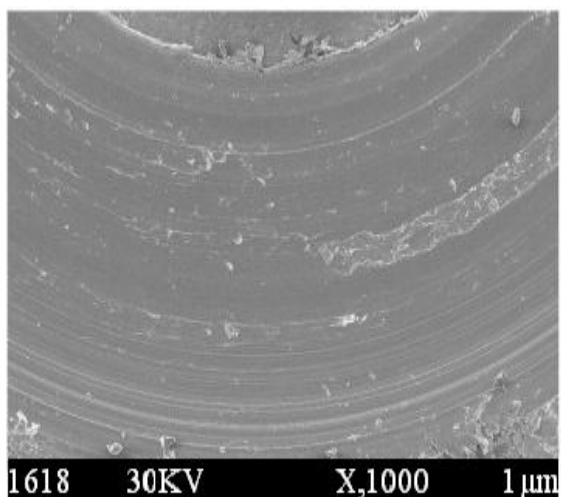


Figure 2.d .SEM PHOTOS OF MILD STEEL IN THE PRESENCE OF CHTU (100 ppm) IN 1M H<sub>2</sub>SO<sub>4</sub>

### Conclusions

1. Cyclohexyl thiourea inhibits the corrosion of mild steel in both acids, but shows a better performance in 1N H<sub>2</sub>SO<sub>4</sub>.
2. The inhibition of corrosion of mild steel in both the acids, by the compound is under cathodic control.
3. The presence of inhibitor in both the acids is found to enhance the extent of ingress of hydrogen through mild steel.
4.  $R_t$  and  $C_{dl}$  values obtained from impedance measurements confirm the better performance of the compound.
5. The adsorption of the compound on mild steel surface obeys Temkin's adsorption isotherm.

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