

The influence of Isopropyl thiourea (ISPT) on the corrosion and hydrogen permeation through mild steel in acidic solutions.

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Abstract: The influence of Isopropyl thiourea (ISPT) on corrosion and hydrogen permeation through mild steel in 0.5M H₂SO₄ and 1M HCl has been studied using weight loss measurements and various electrochemical techniques. Isopropyl thiourea (ISPT) is found to be more inhibitive in H₂SO₄ than in HCl. Potentiodynamic polarization studies clearly prove the fact that this compound behaves as a mixed inhibitor; but predominantly as a cathodic inhibitor. Hydrogen permeation studies and AC impedance measurements also indicate an improved performance of the compound in H₂SO₄. The adsorption of this compound on the mild steel surface obeys Temkin's adsorption isotherm.

Keywords: Corrosion inhibitor, Isopropyl thiourea, hydrogen permeation.

1. 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 [4]. 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 isopropyl 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.

2. MATERIALS AND METHODS

Mild steel specimens of compositions, C = 0.07%, P = 0.08%, Si = 0%, S = 0%, Mn = 0.34% and Fe remainder, and of size 5 x 2 x 0.025 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 cm² was used for galvanostatic polarisation and AC impedance measurements. All the inhibitors were preliminarily screened by a weight loss method described earlier. [9] Both cathodic and anodic polarisation curves were recorded potentiodynamically (1 mVs⁻¹) 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/Hg₂Cl₂/1 N HCl and Hg/HgSO₄/1 N H₂SO₄ 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_{dl}) and charge transfer resistance values (R_c) 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-V IS-NIR Spectrometer, Hitachi, Japan).

3. RESULTS AND DISCUSSION

3.1. weight loss and gasometric measurements

Table I gives the values of inhibition efficiency for different concentrations of isopropyl thiourea for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ 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 H₂SO₄. 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 case of HCl the stronger adsorption of the chloride ions on the metal surface leaves less space for organic molecules to get adsorbed. So in H₂SO₄, 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 [9].

The inhibition of corrosion brought about by isopropyl 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 isopropyl 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.

3.2. Galvanostatic Polarisation studies

Table II(a) and II (b) give values of corrosion kinetic parameter such as Tafel slopes (b_a and b_c), corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency obtained from galvanostatic polarization curves for mild steel in 1M HCl and 0.5 M H₂SO₄ containing different concentrations of isopropyl thiourea. 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]. It can also be seen from these tables that increasing concentrations of isopropyl thiourea enhances the values of both b_a and b_c , but the values of b_c are enhanced to great 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 isopropyl thiourea brings down 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 galvanostatic studies are well in agreement with each other.

Table I. Values of inhibition efficiency for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ in the presence of different concentrations of Isopropyl thiourea obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (mM)	Inhibition efficiency (%)			
	HCl	H ₂ SO ₄	Weight loss studies	Gasometric measurements
1	83	83.6	94.2	94.7
5	85.3	85.9	95.3	95.9
10	89.7	90.5	90.9	91.6
50	93.4	93.8	96.7	97.2

Table II.a- Corrosion kinetic parameters of mild steel in 1M HCl in the presence of different concentrations of Isopropyl thiourea obtained from galvanostatic 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	65	120	2.80	---
1	-494	73	126	0.47	83
10	-488	76	136	0.31	89.3

Table II.b Corrosion kinetic parameters of mild steel in 1M H₂SO₄ in the presence of different concentrations of Isopropyl thiourea obtained from galvanostatic 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	-910	70	130	2.20	---
1	-894	70	136	0.35	85.2
10	-885	76	136	0.31	88.7

3.3. 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 III. Hydrogen permeation current for mild steel in 1M HCl is more, because of the aggressive nature of chloride ions. It can be seen from the table that the presence of isopropyl 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, invariably the product of decomposition of isopropyl thiourea is H₂S, which is evolved on the metal surface. Its

formation can be detected by radiometric measurements, if labeled thiourea derivatives are used [15]. The whole process takes place in two stages. In the first stage, isopropyl 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 undergoes chemical changes. The molecule usually decomposes with the formation of H₂S 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 isopropyl 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.

3.4. Impedance Studies

Values of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are shown in Table IV. It can be seen in table that the values of R_t is found to increase with increase in concentration of isopropyl thiourea in both the acids. Values of double layer capacitance are found to be more for 1M HCl than for 0.5M H₂SO₄. It is found that values of C_{dl} are brought down by increasing concentrations of isopropyl

thiourea 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 $\log C_i$ gives a straight line showing that the adsorption of ISP T 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.

3.5. SEM

SEM photographs obtained for mild steel surface immersed in 1N HCl and 1N H₂SO₄ solutions for 3 hrs in the absence and presence of 100 mM of ISP T are shown in Fig 1 (a, b, c & d). It can be observed from Fig 1a & Fig 1b, that the specimen surfaces were strongly damaged in the absence of the inhibitor. SEM image of inhibited mild steel specimen (Fig. 1c & 1d) reveals that a good protective adsorbed film is formed on the specimen's surface, which suppresses the rate of corrosion, being responsible for the inhibition.

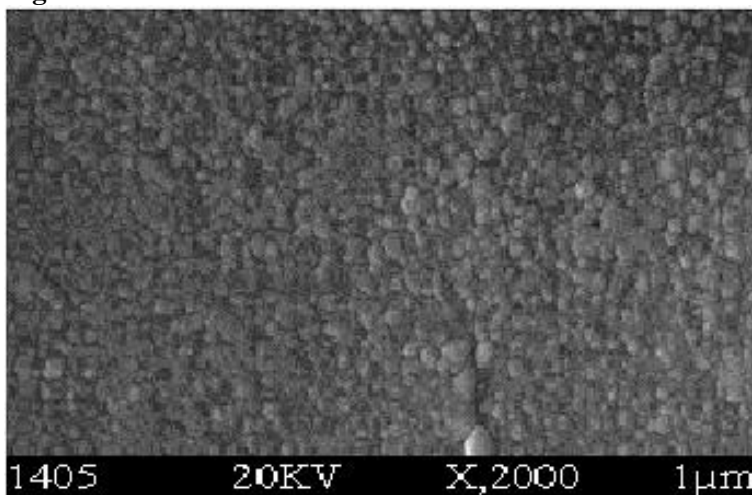
Table III. Values of permeation current for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ in the presence of different concentrations of Isopropyl thiourea.

Concentration of Inhibitor (mM)	Steady state permeation current (μ A)	
	1M HCl	1M H ₂ SO ₄
Blank	22.8	12.5
1	25.5	12.6
10	23.9	13.5
50	24.2	14.6

Table IV. Impedance parameters for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ in the presence of different concentrations of Isopropyl thiourea.

Concentration of Inhibitor (mM)	HCl		H ₂ SO ₄	
	Charge Transfer resistance (R _t)	Double layer capacitance (C _{dl}) μF.cm ⁻²	Charge Transfer resistance (R _t)	Double layer capacitance (C _{dl}) μF.cm ⁻²
Blank	44	243	6.4	184
1	31	170.5	32	187.4
10	42.6	135.5	44	131.2
50	70.7	120.9	78.4	109.6

Fig.1a. SEM PHOTOS OF MS 1N HCL



4. CONCLUSION

1. Isopropyl thiourea inhibits the corrosion of mild steel in both acids, but shows a better performance in 0.5M H₂SO₄.
2. The inhibition of corrosion of mild steel in both the acids, by the compound is under cathodic control.
3. The presence of ISPT in both the acids is

found to enhance the extent 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.

Fig.1b. SEM PHOTOS OF MS IN 1 M H₂SO₄

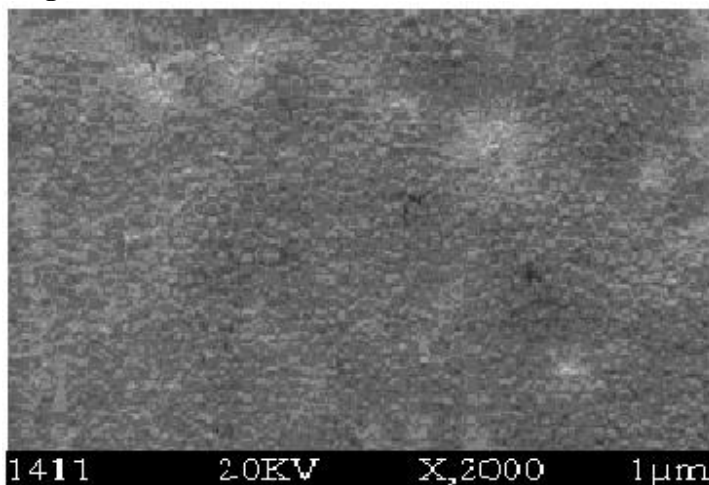


Fig.1c. SEM PHOTOS OF ISPT IN IN HCl

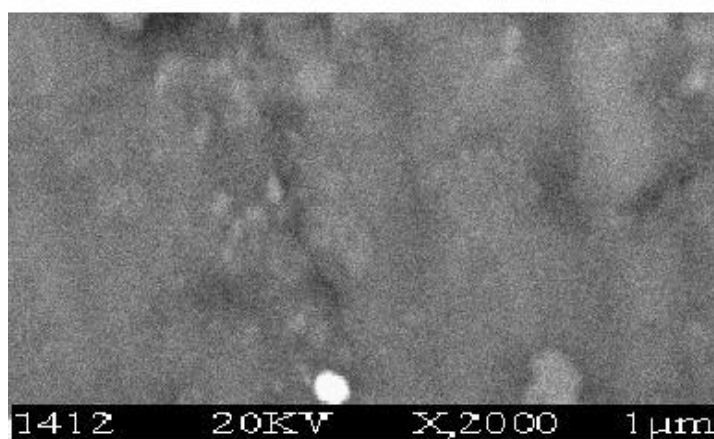
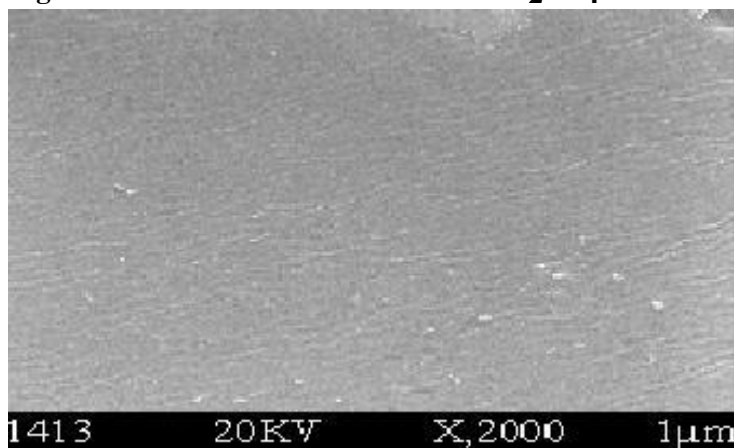


Fig.1d. SEM PHOTOS OF ISPT IN 1N H₂SO₄



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