

Corrosion Inhibition of Stainless Steel in Hydrochloric Acid by N - (2-mercaptophenyl) -N' - phenyl Thiourea

Ramadev Herle^{1*}, Prakash Shetty², S. Divakara Shetty¹
and U. Achutha Kini¹

¹*Department of Mechanical Engineering,*

²*Department of Printing & Media Engineering,*

Manipal Institute of Technology, Manipal University,

Manipal -576104, Karnataka, India.

**Corresponding Author E-mail: ram.herle@manipal.edu*

Abstract

The inhibition effect of N - (2-mercaptophenyl) -N' - phenyl thiourea (MPTU) on the corrosion of 304 SS in 2 N HCl medium has been investigated by potentiodynamic polarization and weight loss methods. The results obtained reveal that MPTU is an efficient mixed inhibitor with efficiency of greater than 92% in the temperature range studied. The adsorption of this inhibitor on the 304 SS surface obeys Temkeins adsorption isotherm, and the inhibition is governed by physisorption mechanism. The influence of parameters like temperature and inhibitor concentration on the corrosion rate of 304 SS has also been investigated. The thermodynamic parameters deduced for the adsorption process reveal a strong interaction and spontaneous adsorption of MPTU on the alloy steel surface.

Keywords: 304 SS, Hydrochloric acid, Mixed inhibitor, Potentiodynamic polarization, Adsorption, Activation energy.

Introduction

Stainless steels are used in various applications such as in the oil and petrochemical industry and as parts of desalination plants.¹ Stainless steels are susceptible to uniform corrosion only in highly acid environments.² The investigation of the inhibition of corrosion of steel is always a subject of high theoretical as well as practical interest. Some of the important areas of application of mineral acids are industrial acid

cleaning, acid pickling, acid descaling and oil well acidizing. Because of the aggressiveness of acids, inhibitors are often used to reduce the rate of dissolution of metals. Generally, adsorption results in effective blocking of the active sites of metal dissolution and / or hydrogen evolution, thus diminish the overall corrosion reaction. The modes of adsorption depend mainly on the chemical structure of the inhibitor, the chemical composition of the solution, the nature of the metal surface and the electrochemical potential of metal – solution interface.³ The corrosion of stainless steels in acid solutions with the organic sulphur containing compounds has been studied by many authors.⁴ The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on the metal surface.⁵ As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are likely the potential corrosion inhibitors⁶. Zucchi et.al. studied the inhibitive action of some series of organic compounds containing N and S against corrosion of steels in 4 N HCl solution⁷. Cheng et.al. reported the use of thiourea and phenyl thiourea as inhibitors for the corrosion of ferrite and austenitic stainless steel in sulphuric acid medium⁸. Abdallah studied the effect of rhodanine azosulpha drugs on the corrosion behaviour of 304 SS in 1 M HCl solution⁹.

In the present work, inhibiting action of N - (2-mercaptophenyl) -N' - phenyl thiourea (MPTU) on the corrosion of 304 SS in 2 N HCl medium has been investigated by potentiodynamic polarization and weight loss techniques.

Experimental

Specimen

Stainless steel (304 SS) specimens with chemical composition as given in Table 1 were used in the present investigation. The specimens were mechanically polished with emery papers of 1/0 – 5/0 grade, thoroughly cleaned with soap water, rinsed with distilled water and then with alcohol and finally dried in air.

Table 1: The Chemical composition of 304 SS.

Elements	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	V
Weight (%)	0.03	0.54	1.40	0.03	0.006	18.02	0.50	8.00	0.013	0.55	0.07

Corrosion medium

AR grade HCl (Merck) and double distilled water were used to prepare 2 N HCl solution as the corrosion medium.

Inhibitor

N - (2-mercaptophenyl) -N' - phenyl thiourea (MPTU) was synthesized by following the reported procedure¹⁰. The compound was recrystallized by ethanol and its purity was checked by IR spectra, elemental analysis and melting point ($161 \pm 1^\circ\text{C}$). The inhibitor was used in the concentration range of 25 – 400 ppm.

Methodology

Polarization Method: The electrochemical studies were performed at room temperature ($30 \pm 1^\circ\text{C}$) using a Wenking Potentiostat (LB 95L) and a three electrode cell. A platinum electrode was used as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The steady state open circuit potential (OCP) with respect to saturated calomel electrode was noted at the end of 25 – 30 minutes. The Tafel extrapolation studies were made by varying the potentials from -250 mV versus OCP to +250 mV versus OCP at a scanning rate of 20 mV from the cathodic side and the corrosion currents were noted. The experiments were repeated at 40, 50 and 60°C .

The Tafel plots of potential versus $\log I$ were drawn. The corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) were determined from the point of intersection of the extrapolated linear anodic and cathodic regions. The corrosion rate (CR) and the percentage inhibition efficiency (%IE) were calculated. The results obtained were cross-checked by linear polarization and weight loss methods.

Weight loss method: The weight of 304 SS specimen after polishing with emery papers of different grades was measured accurately before exposing it to 100 ml of uninhibited and inhibited and medium solution. After 48 hours of the immersion, the specimen was withdrawn, washed with double distilled water, rinsed with ethonol, dried, polished gently with the emery paper and weighed. From the weight loss the % IE at each inhibitor concentration was calculated using the following equation.⁹

$$\text{IE} = (1 - w_{\text{add}}/ w_{\text{free}}) \times 100$$

Where, w_{add} and w_{free} are the weight loss of the specimen in the presence and absence of MPTU respectively.

Results and Discussion

The inhibition efficiency and the corrosion rate determined by the potentiodynamic polarization technique, under the given experimental conditions are presented in Tables 2. The corrosion rate (CR), the degree of surface coverage (θ) and the percentage inhibitor efficiency (% IE) of 304 SS were calculated using the following relations⁶.

$$\text{Corrosion Rate (mpy)} = \frac{0.1288 \times \text{Eq. wt} \times i_{\text{corr}}}{D} \text{ -----} \quad (1)$$

Where, i_{corr} = Corrosion current density in $\mu\text{A}/\text{cm}^2$,

Eq. wt = specimen equivalent weight in g.

D = specimen density in g/cc.

$$\theta = \frac{(CR_o - CR)}{CR_o} \text{ -----} \quad (2)$$

$$\% IE = \frac{(CR_0 - CR)}{CR_0} \times 100 \text{ -----} \quad (3)$$

where, CR_0 and CR are the corrosion rates in the absence and presence of the inhibitor respectively.

Table 2: Tafel extrapolation results for the corrosion inhibition of 304 SS in 2 N HCl at different concentrations of MPTU at different temperatures.

Temperature °C	Inhibitor Concentration c (ppm)	$E_{\text{corr.}}$ (mV)	i_{corr} (μ A/ cm^2)	CR (mpy)	IE (%)
30	0	-395	170.20	76.52	-
	25	-385	47.05	21.15	72.36
	50	-380	40.04	18.00	76.47
	100	-380	33.03	14.85	80.59
	200	-378	26.03	11.70	84.71
	300	-377	19.02	8.55	88.82
	400	-378	28.03	12.60	83.53
40	0	-388	230.23	103.50	-
	25	-380	55.06	24.75	76.08
	50	-380	46.05	20.70	79.99
	100	-385	39.04	17.55	83.04
	200	-385	31.53	14.18	86.30
	300	-380	24.02	10.79	89.57
	400	-375	29.03	13.05	87.39
50	0	-384	380.38	171.02	-
	25	-380	99.09	44.55	73.95
	50	-378	89.09	40.05	76.58
	100	-375	75.07	33.75	80.27
	200	-380	67.07	30.15	82.37
	300	-384	58.06	26.10	84.74
	400	-380	63.06	28.35	83.42
60	0	-390	560.56	252.02	-
	25	-388	160.16	72.01	71.43
	50	-390	140.14	63.01	74.99
	100	-388	125.13	56.26	77.68
	200	-385	110.11	49.50	80.36
	300	-385	90.09	40.50	83.93
	400	-383	100.10	45.01	82.14

The results obtained from the weight loss measurements are in good agreement with those obtained from the Tafel and linear polarization methods.

The inhibition effects of N - (2-mercaptophenyl) -N' - phenyl thiourea (MPTU) on the corrosion of 304 SS in 2 N HCl solutions, studied by potentiodynamic polarization techniques at different temperatures are shown in Table 2. It is observed from the polarization curves (Fig.2) and the results (Table 2), that there is not much change in corrosion potential (E_{corr}) values at different concentrations of inhibitor. This indicates that the compound investigated acts as mixed inhibitor in HCl solution. It is also observed from the results that the compound shifts the polarization curves to lower current density values.

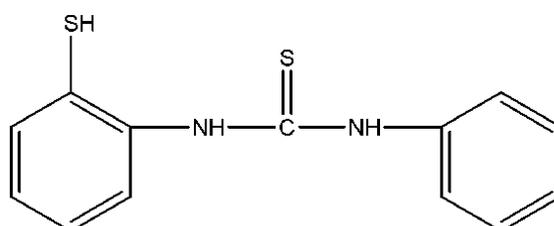


Figure 1: Structural formula of N - (2-mercaptophenyl) -N' - phenyl thiourea.

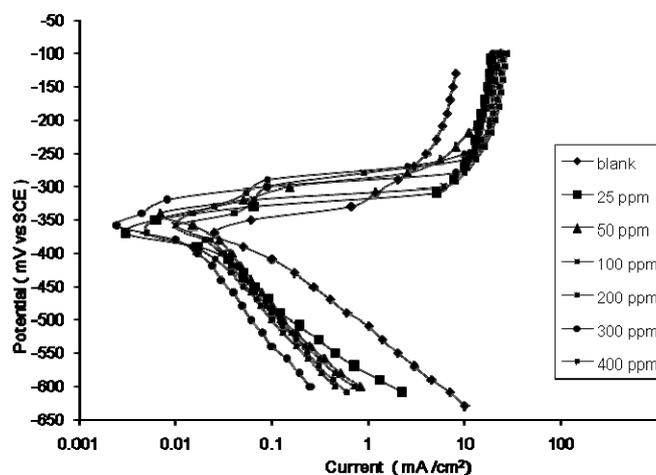


Figure 2: Potentiodynamic polarization curves for 304 SS in 2 N HCL at 30°C with & without Inhibitor.

The increase in efficiency may be due to the blocking effect of the surface by both adsorption and film formation mechanism, which decreases the effective area of corrosion attack. The results confirm that MPTU reduces corrosion rates to a significant extent, showing inhibition efficiency values of over 92% in 2 N HCl. The excellent performance exhibited by the compound may be due the presence of protonated form of N and S atoms of compound which makes it adsorbed quickly on the metal surface, thus forming an insoluble stable film on the surface of 304 SS.

Kinetic parameters for the corrosion of 304 SS

The thermodynamic parameters for the corrosion of 304 SS in the presence of inhibitor (at 300 ppm) is shown in Table 3. The activation energy (E_a), the Gibbs free energy of adsorption (ΔG_{ads}) and equilibrium constant (K) are calculated using following relations.¹¹

$$\ln (r_2/r_1) = - E_a \times \Delta T / (R \times T_2 \times T_1) \text{ -----} \quad (5)$$

Where, r_1 and r_2 are the corrosion rates at temperature T_1 and T_2 respectively and ΔT is the difference in temperatures.

$$\Delta G_{ads} = - R \times T \times \ln(55.5K) \text{ -----} \quad (6)$$

$$K = \theta / c(1-\theta) \text{ -----} \quad (7)$$

Where, R is the universal gas constant and 55.5 is the concentration of water in mol/L, θ is the degree of surface coverage of the metal surface and c is the concentration of the inhibitor in ppm.

Table 3: The results of weight loss method for the corrosion of 304 SS in 2N HCl medium with and without inhibitor at room temperature (30°C).

Medium	Inhibitor Concentration c(ppm)	IE (%)
2 N HCl	0	72.36
	25	76.47
	50	80.59
	100	84.71
	200	88.82
	300	83.53
	400	72.36

Table 4: Thermodynamic parameters for the corrosion of 304 SS in 2 N HCl.

Concentration of MPTU	Activation Energy, E_a (kJ/mol)	Gibbs free energy of adsorption $-\Delta G_{ads}$ (kJ/mol)			
		30° C	40° C	50 °C	60 °C
Blank	39.72	-	-	-	-
300 ppm	42.49	32.45	33.92	34.08	35.11

The higher value of E_a in the inhibited solution indicates that the MPTU retards the corrosion process more effectively at lower temperature. The negative values of ΔG_{ads} indicate spontaneous adsorption and strong interaction of the inhibitor molecules on to the surface of 304 SS. Since the values of ΔG_{ads} obtained are less than

40 kJ/ mol⁻¹, the adsorption of inhibitor molecules on the 304 SS surface takes place by physisorption mechanism.¹¹

Adsorption Mechanism

To understand the mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbates on the metal surface must be known. The surface coverage values for different concentrations of MPTU from the acid solution were tested graphically by fitting to various adsorption isotherms. The plot of degree of surface coverage, θ versus $\log c$ (Fig.3) for different concentrations of the compound shows a straight line indicating that the adsorption of the compound on the steel surface follows Temkins adsorption isotherm. The applicability of Temkins adsorption isotherm verifies the assumption of monolayer adsorption on uniform homogeneous metal surface with an interaction in the adsorption layer¹². Monolayer adsorption resulted in a decrease in surface area available for cathodic and anodic reactions.

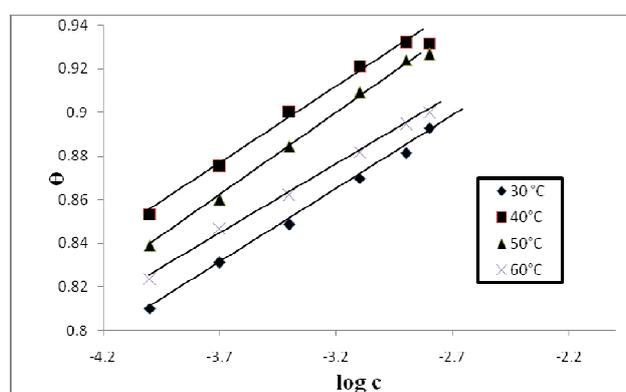


Figure 3: Temkin's adsorption isotherm for MPTU in 2 N HCl at different temperatures.

Conclusions

1. MPTU has proved to be an efficient mixed inhibitor for the corrosion of 304 SS in HCl solution.
2. Polarization behavior of 304 SS in the presence of MPTU showed drastic reduction in the corrosion rate.
3. The % IE was found to increase by increasing the inhibitor concentration up to a critical concentration of 300 ppm.
4. The inhibition of corrosion of 304 SS in HCl medium was found to obey the Temkin's adsorption isotherm and it is governed by physisorption mechanism.
5. The study reveals that the presence of MPTU increases the activation energy of the corrosion process.
6. The negative values of ΔG_{ads} indicate the spontaneous adsorption and strong interaction of the inhibitor molecules on the surface of 304 SS.

References

- [1] Hermas A.A., Morad M.S., Wahdan M.H. (2004) *Jr. of Appl. Electrochemistry* 34, pp. 95.
- [2] Pohjanne P., Carpen L., Hakkarainen T. (2008) *Jr. of Constructional steel research*, 64, pp. 1325.
- [3] Benabdellah M., A.Dafali, Hammouti B. (2007) *Chem, Engg. Comm.* 194, 1328.
- [4] Cheng X.L., Ma H.Y., Z.M. Yao. (1999) *Corros. Sci.* 41, 321.
- [5] Rafaey S.A.M., Taha F. (2004) *Appl.Surf.Sci.* 236, 175.
- [6] Divakara Shetty S, Prakash Shetty, Sudhakara Nayak H.V.(2005) *Ind. Jr. Chem. Technol.* 12, 462.
- [7] Fabrizio Zucchi, Giordano Trabanelli (1992) *Corros.Sci.* 33, 1135.
- [8] Cheng X. L. , Chen S. H. (1999) *Corros. Sci.* 41, 321.
- [9] Abdallah M. (2002), *Corros. Sci.*, 44 , 717.
- [10] Moore M.L., Crossley F.S. (1962), *Organic synthesis*, Vol.3, E. C. Horning (Ed), John Wiley and Sons, New York, pp..599.
- [11] Ramesh Salian V., Airody Vasudeva Adhikari (2008), *Corros. Sci.*, 50, pp. 55.
- [12] Sathyanarayana S. (2005), *Appl. Surf. Sci.*, 241, pp. 477.