Corrosion Inhibition of 304 SS in Hydrochloric Acid Solution by N – Furfuryl N'– Phenyl Thiourea

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Abstract

The inhibition of corrosion of 304 SS in 2 N HCl solutions by N – furfuryl – N' phenyl thiourea (FPTU) has been investigated using potentiodynamic polarization techniques. The results obtained reveal that FPTU performs excellently as anodic inhibitor (IE> 93%) for 304 SS in HCl solution. The inhibitor functions through adsorption following Temkin's adsorption isotherm, and the inhibition was governed by physisorption mechanism. The thermodynamic parameters deduced for the adsorption process reveal spontaneous adsorption of the compound on the alloy steel surface.

Keywords: 304 SS, hydrochloric acid, inhibition, FPTU, adsorption.

Introduction

Corrosion is the deterioration of essential properties of a material due to reactions with its surroundings. Millions of dollars are lost each year because of corrosion. Much of this loss is due to the corrosion of iron and steel, although many other metals may corrode as well [1]. Inhibitors are often added to chemical cleaning and pickling process in dilute acids at moderate temperature. Inhibitors must be stable and effective even under severe conditions in hot concentrated acid [2]. The effect of organic nitrogen compounds on the corrosion behavior of iron and steel in acidic solutions has been well documented [3]. It has been reported that many heterocyclic compounds containing heteroatoms like N, O, S, have been proved to be effective inhibitors for the corrosion of steel in acid media [4]. The

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inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the film formed on the metal surface [5]. It has been observed that the adsorption depends mainly on certain physico-chemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and π orbital character of donating electrons and also on the electronic structure of the inhibitor [6]. It has been accepted that the corrosion inhibition process results from the formation of an organic inhibitor film on the metal surface by the compounds containing heteroatoms like N, O, S, and hence thioureas have proved to be fairly effective in corrosion control [7]. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are likely the potential corrosion inhibitors [8]. Selection of effective corrosion inhibitors is very important for an application in which inhibitors are selected based on what kind of metal or alloy and corrosive environment are used. Effectiveness of the organic inhibitors depends on the extent of adsorption and fraction of surface area covered on metal surface [9]. Zucchi et al. [10] studied the inhibitive action of some series of organic compounds containing N and S against corrosion of steels in 4 N HCl solution and found that they act as anodic inhibitor. Cheng et al. [11] reported the use of thiourea and phenyl thiourea as inhibitors for the corrosion of ferrite and austenitic stainless steel in sulphuric acid medium. The results show that the covering effect of phenylthiourea on the metal surface is better than that of thiourea, and the corrosion rate of stainless steels decreased more remarkably in solutions with phenylthiourea than in solutions with thiourea. Abdallah [12] studied the effect of rhodanine azosulpha drugs on the corrosion behaviour of AISI 304 stainless steel in 1 M HCl solution. Rhodanine azosulpha drugs act as mixed inhibitors and the maximum % IE is 87 %.

AISI 304 SS is the basic chromium-nickel stainless steel which has found wide applications in a variety of industries like paper, automobile, petroleum industries, etc., because of its important characteristics such as fabricability, durability, mechanical strength, corrosion resistance, cost and availability [12]. This paper deals with the study of the inhibiting effect of N – furfuryl – N′– phenyl thiourea (FPTU) on the corrosion behaviour of 304 SS in 2 N hydrochloric acid medium at four different temperatures and at five levels of inhibitor concentration, by potentiodynamic polarization techniques. The choice of FPTU as inhibitor in the present investigation is based on the fact that substituents to thiourea increase further its electron density for adsorption on metal surface; moreover, it can be synthesized conveniently from relatively cheap raw materials.

Experimental
Material
304 SS specimen (circular coupons of diameter 1.12 cm with area exposed as 0.999 cm^2) with chemical composition as given in Table 1 was used in the present study. One flat surface of the specimen was 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. Chemical composition of 304 SS.

Elements	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	V
Weight(%)	0.07	0.54	1.40	0.03	0.006	18.02	0.50	8.00	0.013	0.15	0.07

Corrosion medium
Analytical reagent grade HCl (Merck) and double distilled water were used for preparing test solution of 2 N HCl for all experiments.

Inhibitor
The compound, N - furfuryl – N$'$ - phenyl thiourea ($C_{12}H_{12}ON_2S$), Fig. 1, was used as inhibitor for investigating the corrosion behavior of 304 SS. The melting point of the compound used is 135 °C [8]. The results of elemental analysis of the compound are given in Table 2. The compound was used in the concentration range of 50 – 400 ppm.
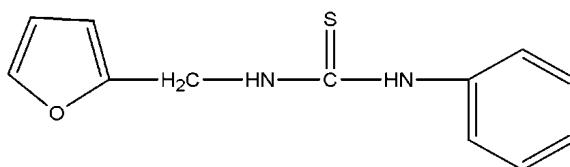
Figure 1. Structural formula of N – furfuryl – N$'$– phenyl thiourea.

Table 2. Results of elemental analysis of FPTU.

Elements	C	H	O	N	S
Calculated (%)	62.04	5.21	12.06	6.89	13.80
Found (%)	61.88	5.19	12.02	6.92	13.76

Polarization studies
By using a Wenking Potentiostat (LB95L) and a three electrode cell, electrochemical studies were performed. 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 corrosion rates are determined both by linear polarization and Tafel extrapolation techniques. The experiments are repeated at temperatures of 30, 40, 50 and 60 °C.

Linear polarization technique
Linear polarization studies were carried out in the potential (E) range of -20 mV vs. OCP to +20 mV vs. OCP in steps of 5 mV/min from the cathodic side and the corresponding steady state corrosion currents (I) were noted. The graphs of E vs. I are drawn, and from the slope of the graph the corrosion current density (i_{corr}) and the corrosion rate (CR) are calculated using the following equations [13, 14].

$$i_{corr} = (0.026 \times 10^6) / (slope \times A) \qquad (1)$$

$$\text{Corrosion rate (mpy)} = \frac{0.1288 \times Eq.wt \times i_{corr}}{D} \qquad (2)$$

where, A = exposed area of the specimen in cm^2 (0.999 cm^2); i_{corr} = corrosion current density in μA/cm^2; Eq.wt = specimen eq.wt. in g (27.925 g); D = specimen density in g/cc (8 g/cm^3).
Also,

$$\text{Degree of surface coverage, } \Theta = \frac{(CR_O - CR)}{CR_O} \qquad (3)$$

$$\text{Percentage inhibiton efficiency, } \% \, IE = \frac{(CR_0 - CR)}{CR_0} \times 100 \qquad (4)$$

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

Tafel extrapolation technique
Tafel extrapolation studies were made by varying the potentials from -250 mV vs. OCP to +250 mV vs. OCP in steps of 20 mV from the cathodic side and the corrosion currents were noted. The Tafel plots of potential vs. 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) was calculated using equation (2). Experiments were repeated for each of the variables, namely temperature and concentration of the inhibitor.

Results and discussion
The inhibition effects of N – furfuryl – N' – phenyl thiourea (FPTU) on the corrosion of 304 SS in 2 N hydrochloric acid solution, studied by potentiodynamic polarization techniques at different temperatures, are shown in Tables 3 and 4. It is observed from the polarization curves (Fig. 2) and the results (Tables 3 and 4), that the presence of FPTU shifted the values of corrosion potential (E_{corr}) to more anodic potential. This indicates that the compound investigated acts as anodic inhibitor in HCl solution. It is also observed from the results that the compound shifts the polarization curves to lower current density values.

Table 3. Linear polarization results for the corrosion inhibition of 304 SS in 2 N HCl at different concentrations of FPTU and at different temperatures.

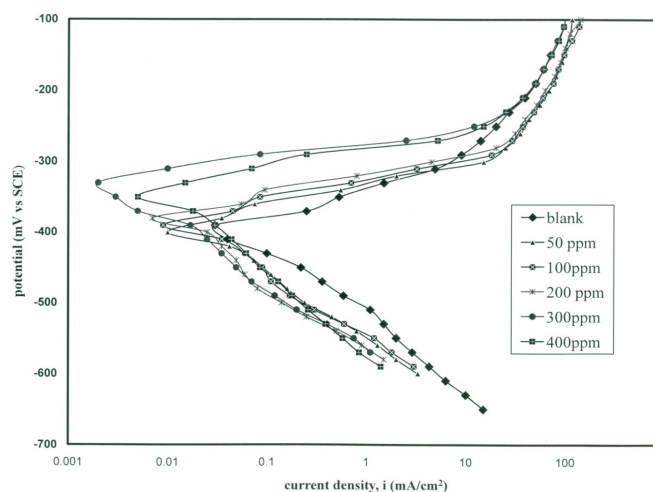| Temperature °C	Inhibitor concentration c (ppm)	OCP (mV)	i_{corr} ($\mu A/cm^2$)	CR (mpy)	IE (%)
	0	-375	156.16	70.21	-
	50	-360	20.82	9.36	86.67
	100	-360	15.62	7.02	90.00
30	200	-340	15.36	6.91	90.16
	300	-330	13.01	5.85	91.67
	400	-340	15.62	7.02	90.00
	0	-370	234.23	105.31	-
	50	-360	26.94	12.11	88.50
	100	-360	26.03	11.70	88.89
40	200	-350	20.81	9.36	91.11
	300	-350	18.22	8.19	92.22
	400	-360	20.82	9.36	91.11
	0	-370	364.36	163.81	-
	50	-360	57.26	25.74	84.28
	100	-350	37.74	16.97	89.64
50	200	-350	33.83	15.21	90.71
	300	-360	31.23	14.04	91.43
	400	-370	36.30	16.32	90.04
	0	-360	546.54	245.72	-
	50	-360	100.87	45.35	81.54
	100	-360	72.87	32.76	86.67
60	200	-350	70.27	31.59	87.14
	300	-360	57.26	25.74	89.52
	400	-370	62.46	28.08	88.57

The increase in efficiency may be due to the blocking effect of the surface by both adsorption and film formation mechanisms, which decrease the effective area of corrosion attack. The results confirm that FPTU reduces corrosion rates to a significant extent, showing inhibition efficiency values of over 93% in 2 N HCl. The excellent performance exhibited by the compound may be due to the presence of the protonated form of N and S atoms of the compound which makes it to adsorb quickly on the metal surface, thus forming an insoluble stable film on the surface of 304 SS. Since sulphur is less electronegative than nitrogen and has two electron pairs available for co-ordination, the bonding between the inhibitor molecule and 304 SS surface probably occurs through a sulphur atom.

The effect of the temperature on % IE is shown in Tables 3 and 4. It is evident from the results that the corrosion current density and corrosion rate values are increased significantly with increasing temperature in uninhibited solutions. It is also evident from the results that there is not much noticeable change in the IE with the increase in temperature from 30 to 60 ºC. This indicates that FPTU is insensitive to temperature. The high IE exhibited by FPTU may be attributed to its adsorption on the metal surface through polar groups as well as through π – electrons of the double bond. This leads to greater coverage of the metal surface by FPTU, thereby resulting in higher IE. The inhibiting effect of FPTU can be attributed to its parallel adsorption at the metal solution interface. The parallel adsorption takes place owing to the presence of one or more active centres for

adsorption. The values of IE marginally increased from 30 ºC to 40 °C in HCl solution.

Table 4. Tafel extrapolation results for the corrosion inhibition of 304 SS in 2 N HCl at different concentrations of FPTU and at different temperatures.

Temperature °C	Inhibitor concentration c (ppm)	$E_{corr.}$ (mV)	i_{corr} ($\mu A/cm^2$)	CR (mpy)	IE (%)
	0	-395	170.20	76.52	–
	50	-376	22.02	9.90	87.06
	100	-371	19.02	8.55	88.82
30	200	-365	16.03	7.21	90.58
	300	-362	13.02	5.85	92.35
	400	-374	18.04	8.11	89.40
	0	-388	230.23	103.50	–
	50	-375	27.03	12.15	88.26
	100	-372	20.02	9.01	91.30
40	200	-363	19.02	8.55	91.74
	300	-360	15.02	6.75	93.48
	400	-366	18.02	8.10	92.17
	0	-384	380.38	171.02	–
	50	-368	47.05	21.15	87.63
	100	-366	40.04	18.00	89.47
50	200	-363	35.04	15.75	90.79
	300	-360	28.03	12.60	92.63
	400	-366	33.03	14.85	91.32
	0	-390	560.56	252.02	–
	50	-375	76.08	34.20	86.43
	100	-370	70.07	31.50	87.50
	200	-364	51.05	22.95	90.89
60	300	-361	47.05	21.15	91.61
	400	-369	54.05	24.30	90.36

Figure 2. Potentiodynamic polarization curves for 304 SS in 2 N HCl at 30 °C in the absence and presence of the inhibitor.
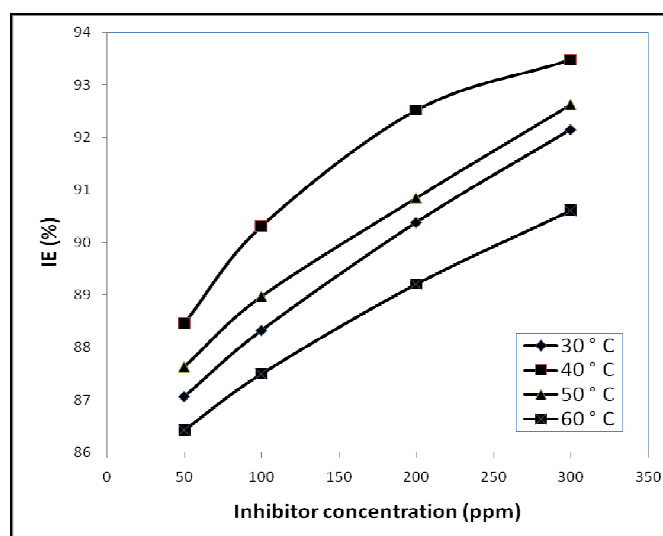
Figure 3. Variation of *% IE* with concentration of the inhibitor in 2 N HCl at different temperatures.

However, IE values marginally decreased with increase in temperature from 50 °C to 60 °C. The decrease in IE and increase in corrosion rates at elevated temperature may be due to desorption of FPTU from the steel surface. Decrease in IE with increase in temperature may be due to the fact that the rate of corrosion is faster than the rate of adsorption [17, 18]. It is also observed from the results that corrosion rate values for 304 SS increase more rapidly with temperature in the absence of the inhibitor. The raise in temperature results in an increase in conductance of aqueous medium and thereby increases the diffusion rate of hydrogen ions on the metal surface. Hence corrosion progresses faster at higher temperatures.

The effect of inhibitor concentration on the percentage inhibition efficiency (*% IE*) is graphically represented in Fig. 3. The *% IE* of the compound was found to increase with increasing concentration of the inhibitor up to a critical concentration (300 ppm). The inhibition was estimated to be superior to 87%, even at concentrations as low as 50 ppm, and the maximum efficiency of 93 % was recorded at 300 ppm. From the graph it is evident that the concentration change had only marginal influence on inhibition efficiency.

Kinetic parameters for the corrosion of 304 SS
The thermodynamic parameters for the corrosion of 304 SS in the presence of the inhibitor (at 300 ppm) are shown in Table 5. Activation energy (E_a), Gibbs free energy of adsorption (ΔG_{ads}), equilibrium constant (K), enthalpy of adsorption ΔH_{ads} and entropy of adsorption ΔS_{ads}, are calculated using the following relations [13, 15]

$$\ln (r_2/r_1) = -E_a \times \Delta T/(R \times T_2 \times T_1) \qquad (5)$$

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

Also,

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

$$K = \theta / c(1-\theta) \qquad (7)$$

$$\Delta S_{ads} = d \, \Delta G_{ads} / dT \qquad (8)$$

$$\Delta H_{ads} = d \, (\Delta G_{ads} / T) / d(1/T) \qquad (9)$$

where R is the universal gas constant, 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 5. Thermodynamic parameters for the corrosion of 304 SS in 2 N HCl.

Concentration of FPTU	E_a (kJ/mol)	Gibbs free energy of adsorption $-\Delta G_{ads}$ (kJ/mol)				Entropy of adsorption $-\Delta S_{ads}$ (Jmol^{-1}K^{-1})	Enthalpy of adsorption ΔH_{ads} (Jmol^{-1})
		30 °C	40 °C	50 °C	60 °C		
Blank	27.36	-	-	-	-	102	2,630
300 ppm	51.09	33.47	34.70	35.56	36.54		

The higher value of E_a in the inhibited solution indicates that the FPTU retards the corrosion process more effectively at lower temperatures. The negative values of ΔG_{ads} indicate spontaneous adsorption of the inhibitor molecules on to the surface of 304 SS. Since the values of ΔG_{ads} obtained are less than 40 kJ/mol, the adsorption of inhibitor molecules on the 304 SS surface takes place by physisorption mechanism [15]. Adsorption at the surface involves no reduction of degrees of freedom (i.e. $\Delta S_{ads} > 0$) (Table 5). The positive values of ΔH_{ads} suggest that the adsorption of FPTU molecules is an endothermic process [16].
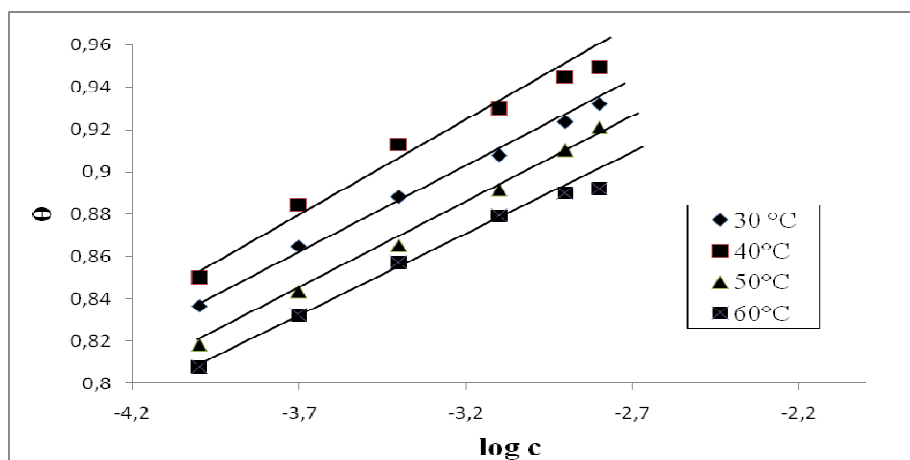
Figure 4. Temkin's adsorption isotherm for FPTU in 2 N HCl at different temperatures.

Adsorption mechanism

To understand the mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbents on the metal surface must be known. The surface coverage values (Θ) for different concentrations of FPTU from the acid solution were tested graphically by fitting to various adsorption isotherms. The plot of θ versus log c (Fig. 4) for different concentrations of FPTU yields a straight line, proving that the adsorption of the compound on the steel surface obeys Temkin's adsorption isotherm [19]. The applicability of Temkin's adsorption isotherm verifies the assumption of monolayer adsorption on a uniform, homogeneous metal surface with an interaction in the adsorption layer. Monolayer adsorption resulted in a decrease in surface area available for cathodic and anodic reactions. The bonding of adsorbed corrosion inhibitors onto the metal surface has been described in terms of concepts of "hard- soft acids and bases" and electrosorption valency [18]. Substituents increase the inhibitive efficiency, probably because of stronger adsorption forces arising from increased electron density due to nucleophilic or electrophilic substituents. Inhibition efficiencies change with the nature of the substituents in the inhibitor molecules as electron densities change at functional groups. It was assumed that the cations of the compound are oriented with the ring structure parallel to the metal surface and adsorbe via a mechanism involving π – electron interaction between the aromatic nucleus and the metal surface [19]. Such interaction will be increased in the presence of multiple bonds. Adsorption can also occur via electrostatic interaction between a negatively charged surface which is provided with a specifically adsorbed anion on Fe and positive charge of the molecule.

Conclusions

1. FPTU has proved to be an efficient anodic inhibitor for the corrosion of 304 SS in HCl solution.
2. The *% IE* was found to marginally increase by increasing the inhibitor concentration up to a critical concentration of 300 ppm.
3. 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.
4. The study reveals that the presence of FPTU increases the activation energy of the corrosion process.
5. The negative values of ΔG_{ads} indicate the spontaneous adsorption of the inhibitor molecules on the surface of 304 SS.

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