Experimental Study on Corrosion Inhibition of 304 SS in Acid Solution

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Abstract

Inhibition is one of the mechanisms used for preventing acid corrosion of metals and alloys. The present work focus on investigating the inhibiting effect of N-furfuryl-N^l-phenyl thiourea (FPTU) on the corrosion of 304 SS in 1M HCl solution using the Tafel extrapolation and electrochemical impedance spectroscopy (EIS) techniques. The study reveals that FPTU acts as a mixed inhibitor, and good inhibition efficiency (> 92%) is observed even at elevated temperatures. The study also reveals that FPTU physically adsorbed on the steel surface, and abeys Temkin's adsorption isotherm. It is evident from the study that the results of the Tafel extrapolation method and electrochemical impedance technique, obtained for the corrosion of 304 SS are in good accord. Since the compound investigated is highly effective in the range of temperatures and concentrations studied, it can be effectively used as inhibitor for mitigating the corrosion of steel in HCl medium.

Keywords: adsorption; activation energy; corrosion; physisorption; 306 SS; Tafel extrapolation; electrochemical impedance spectroscopy.

INTRODUCTION

304 SS has found wide applications in various manufacturing sectors due its good mechanical properties. However, the malfunctioning of the stainless steel occurs owing to pitting corrosion which causes severe technical problems in industries. Therefore, many researchers have shown keen interest in investigating the corrosion behavior of steel in acidic environment. Among the mineral acids, HCl is commonly used for pickling and de-scaling of metal and alloys [1, 2]. It is well known that aqueous corrosion of metals and alloys can be greatly reduced by using inhibitors. The inhibitors are the substances that are added in small quantity to the corrosive medium for decreasing the rate of electrochemical reactions [3]. The inhibition of corrosion of metals or alloys in acid medium is most economical and a trouble-free surface coating technique for enhancing the corrosion resistance of the metals and alloys [4-7].

Generally, the efficient inhibitors are organic compounds containing both N and S atoms. Since the thiourea molecule contains S and N atoms, theourea and its derivatives are the prospective inhibitors for mitigating the metallic corrosion in acid medium. It is observed from the literatures that substituents to thiourea further enhance its electron densities for their adsorption on the metal surface [8-10]. Hence, the present work aims to synthesize N-furfuryl-N^l-phenyl thiourea for predicting the inhibiting action of this compound on the corrosion of 304 SS in 1M HCl solution at different temperatures and inhibitor concentrations by using the Tafel extrapolation and electrochemical impedance spectroscopy methods.

The Tafel plot for the steel specimen can be obtained by polarizing the specimen to about ± 250 mV from the rest potential/open circuit potential, as shown in Fig.1. Extrapolation of the linear region of the anodic and cathodic curves representing the Tafel regions to the corrosion potential will give the corrosion current (I_{corr}). Then the corrosion current density (current per unit area) is calculated and is used for determining the corrosion rate [11, 12].

The electrochemical impedance spectra (EIS) analysis is a powerful tool to determine the mechanism involved in the electrochemical reactions and the values of the kinetic parameters of corrosion mechanism [13]. EIS data is obtained in the form of Nyquist plot which is shown in Fig. 2.
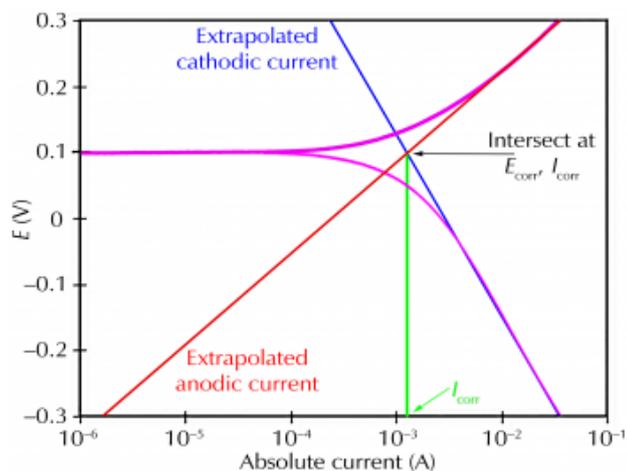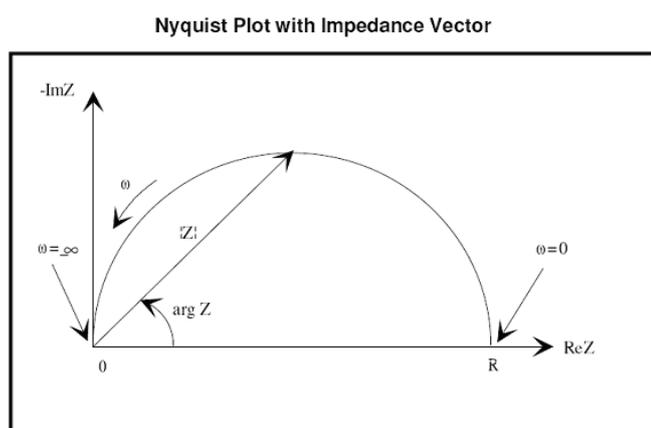
Figure 1: Schematic representation of Tafel plot

Figure 2: Nyquist plot

EXPERIMENTAL

Material preparation

The 304 SS specimen exposed in the acid solution has a bottom surface area of 0.999 cm² is polished with emery papers, cleaned with double distilled water and then dried in air. The specimen with chemical composition (wt. %): 0.03 C; 0.54 Si; 1.40 Mn; 0.033 P; 0.006 S; 18.02 Cr; 0.50 Mo; 8.00 Ni; 0.013 Al; 0.55 Cu; 0.07 V and balance Fe is used in the present work.

Preparation of inhibitor and medium

N-(furfuryl)-N^l-phenyl thiourea (FPTU) is prepared by referring the reported procedure of synthesizing the similar compounds [14]. The compound is purified by ethanol and its purity is checked by elemental analysis. The results of the elemental analysis and the physical properties of the inhibitor studied are given in Table 1 and the structure of the compound is shown in Fig.1. The working medium (1M HCl) is prepared by using AR grade HCl and double distilled water.
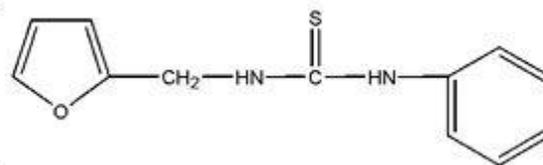

Figure 3: Structure of FPTU

Tafel extrapolation studies

Tafel extrapolation studies are conducted using a Wenking potentiostat (LB 95L). The steady state rest potential (R P) is recorded after 25 - 30 min. The experiments are carried out for the potential range of ±250 mV vs. RP in step of 20 mV from the cathode and the corrosion currents are recorded in the presence and absence of inhibitor at 30°C. The corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) are obtained from the Tafel plot and the corrosion rate is calculated using Eq. 1. The percentage inhibition efficiency (% IE) and the surface coverage (θ) are calculated by using the equations 1 and 2. The repetition of the experiment is carried out at 40, 50 and 60°C, and the Tafel results are validated using electrochemical impedance spectroscopy method.

$$\text{Corrosion rate (mpy)} = \frac{0.129 \times \text{Eq.Wt} \times i_{corr}}{D} \quad (1)$$

Where, i_{corr} = Corrosion current density in mA/cm², Eq.wt = Specimen equivalent weight taken as 27.925 grams, and D = Specimen density taken as 8 g/c.

$$\% \text{ IE} = \left| \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \right| \times 100 \quad (2)$$

Where, i_{corr} and $i_{corr\,(inh)}$ are the corrosion current densities in the absence and presence of inhibitor respectively.

$$\theta = \left| \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \right| \quad (3)$$

Electrochemical impedance spectroscopy

The electrochemical measurement is conducted with a tiny amplitude AC signal of 10 mV over a frequency range of 100 kHz − 0.01 Hz. The Niquisit plot is drawn and the %IE is calculated using the following relation:

$$IE(\%) = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (4)$$

Where, $R_{ct(inh)}$ is the charge transfer resistance in the inhibiting medium and R_{ct} is the charge transfer resistance in the corrosive medium [15,16].

Table 1: Elemental analysis and the physical properties of FPTU

Compound	Molecular Weight (Melting point in °C)	C Found,% (Calcd.,%)	H Found,% (Calcd.,%)	N Found,% (Calcd.,%)	O Found,% (Calcd.,%)	S Found,% (Calcd.,%)
FPTU	232.31 (135)	62.04 (61.88)	5.21 (5.19)	12.06 (12.02)	6.89 (6.92)	13.80 (13.76)

RESULTS AND DISCUSSION

Effect of inhibitor on 304 SS corrosion

Tafel extrapolation results for the corrosion of 304 SS in 1M HCl in the presence and the absence of FPTU at different concentrations and solution temperatures are given in Table 2. It is evident from the Table 2 that IE of the compound is linearly varies with the concentrations of FPTU up to a critical concentration of 1.28 mmol/L, indicating that the rate of corrosion reaction decreases due to the separation of the steel surface from the corrosive medium [17]. After reaching a critical value of inhibitor concentration, % IE of the compound decreases a little bit, which may be due to the desorption of the adsorbed inhibitor molecules from the steel surface. The Fig. 4 illustrates the Tafel extrapolation curves for the corrosion of 304 SS in the absence and presence of FPTU.

Table 2: Tafel extrapolation results for the corrosion of 304 SS

| Temperature(°C)	C (mmol/L)	E_{corr} (mV)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	i_{corr} (mA/cm^2)	CR (mpy)	IE (%)
30	0	-390	65	90	110.10	49.50	-
	0.11	-385	67	96	24.02	10.80	78.18
	0.22	-381	75	98	13.01	5.85	88.18
	0.44	-379	83	102	11.01	4.95	90.00
	0.88	-375	87	106	9.01	4.05	91.82
	1.28	-371	91	112	6.81	3.06	93.62
	1.76	-370	94	118	9.01	4.05	91.82
40	0	-390	65	90	200.20	90.01	-
	0.11	-380	68	93	36.04	16.20	82.00
	0.22	-375	70	96	21.02	9.45	89.50
	0.44	-370	80	104	17.01	7.65	91.50
	0.88	-365	84	106	16.01	7.20	92.00
	1.28	-360	90	110	13.01	5.85	93.50
	1.76	-365	92	118	15.02	6.75	92.50
50	0	-380	65	90	310.31	139.51	-
	0.11	-365	70	94	59.23	26.65	80.90
	0.22	-360	74	96	37.03	16.56	88.13
	0.44	-355	84	103	27.03	12.15	91.29
	0.88	-350	87	107	25.01	11.41	91.82
	1.28	-350	91	112	22.02	9.90	92.90
	1.76	-360	94	120	24.02	10.81	92.25
60	0	-380	43	50	460.46	207.02	-
	0.11	-385	53	60	90.09	40.50	80.44
	0.22	-380	67	64	57.06	25.65	87.61
	0.44	-375	74	68	44.04	19.80	90.44
	0.88	-370	87	70	39.04	17.55	91.52
	1.28	-365	85	74	35.03	15.75	92.39
	1.70	-370	92	72	40.04	18.01	91.30
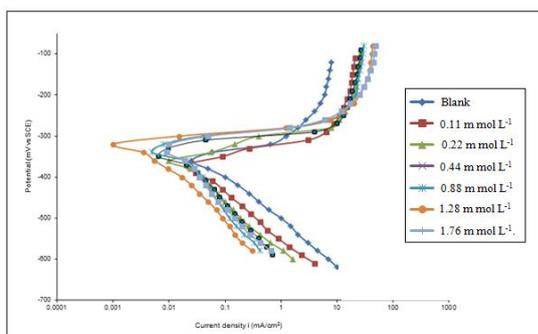
Figure 4: Tafel extrapolation curves for the corrosion of 304 SS at 30° C

In general, if the displacement of corrosion potential (E_{corr}) value with respect to blank solution is more than 85 mV, towards the anodic side or cathodic side, then that inhibitor is considered as anodic or cathodic inhibitor. Or else, the inhibitor is treated as mixed type [18]. From the Fig. 4 and Table 2, it is observed that the maximum shift in E_{corr} in the presence of FPTU is less than 85 mV towards anode with respect to the blank. This confirms that the compound investigated acts as a mixed inhibitor in HCl solution for corrosion of 304 SS. Further, it is noted from the results given in the Table 2 that both the cathodic and the anodic Tafel slopes changes in the presence of FPTU, which also demonstrating that the compound FPTU is a mixed type inhibitor.

The presence of FPTU decreases the corrosion rate to a considerable amount, showing IE values more than 90% in HCl media. The considerable decrease in corrosion loss could be owing to the existence of protonated form of N and S atoms of the compound that makes it adsorbed quickly on the steel surface. [19]. Higher IE exhibited by the compound may be owing to the blocking effect of the surface by both adsorption and film formation mechanism that reduces the effective area of attack. Since the compound investigated exhibited good IE even at very low concentration, it can be efficiently used as inhibitor for inhibiting the corrosion of steel in HCl medium. It is seen from the Table 2 that corrosion rate of 304 SS increases with increase in temperature. This may be due to increase in conductance of the aqueous medium. [20].The study shows that IE of the compound varies marginally with increase in temperature. This indicating that the compound FPTU is insensitive to the temperatures studied.

Electrochemical impedance method

In electrochemical impedance spectroscopy (EIS) method, the impedance responses of the corrosion system are demonstrated in terms of Nyquist plot which is shown in Fig. 5. It is observed from the Fig. 5 that the size semi-circle increases with increase in inhibitor concentration, indicating that the corrosion of 304 SS is controlled mainly by a charge transfer process.
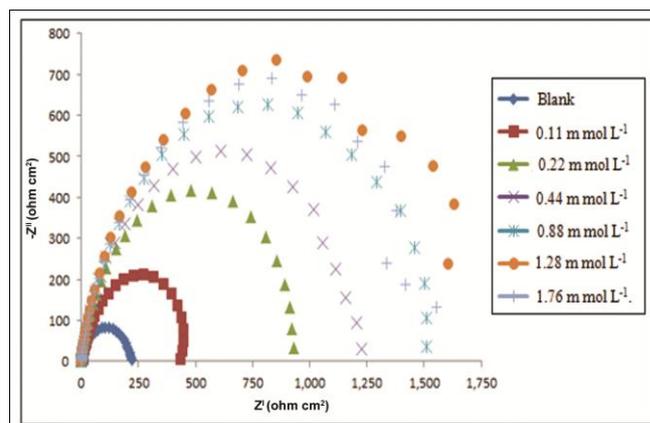

Figure 5: Nyquist plot for the corrosion of 304 SS in 1M HCl at 30 ℃

The results of the impedance spectroscopy method are presented in Table 3. It is evident from the Table 3 that % IE of the compound studied at 30 ℃ is in good agreement with % IE obtained from the Tafel extrapolation method. This confirms the accuracy of the Tafel results deduced for the corrosion of 304 SS in 1M HCl solution.

Table 3: Electrochemical impedance spectroscopy results for 304 SS corrosion at 30 ℃

C (mmol/L)	R_{ct} (ohm/cm^2)	% IE
0	232.40	-
0.11	1036.64	77.58
0.22	1713.63	86.44
0.44	2046.91	88.65
0.88	2568.34	90.95
1.28	2814.62	91.74
1.76	2514.61	90.76

Surface analysis

The surface analysis is also conducted to confirm the experimental results of Tafel extrapolation and electrochemical impedance spectroscopy techniques. The SEM images of 304 SS specimen immersed in 1M HCl solution in the absence and presence of FPTU at 30℃ are shown in Figs. 6 and 7 respectively. The corrosion of 304 SS in HCl medium is most probably due to the anodic dissolution either at the grain boundaries or at the metal - medium interface and also due to the formation of pits at certain regions on the steel surface shown in Fig.6. It is evident from the SEM image (Fig. 7) that the surface of 304 SS immersed in inhibited solution is smoother as compared to the steel surface immersed in uninhibited solution (Fig.6). This clearly signifying that the compound investigated forms a protective layer on the steel surface, and thus, preventing the further attack of acid.
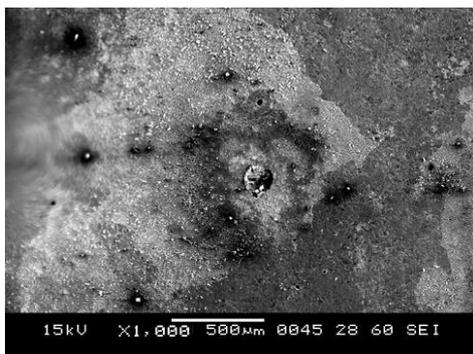
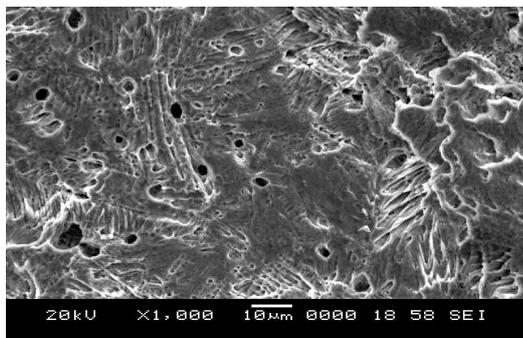**Figure 6:** SEM image of 304 SS exposed to 1 M HCl solution

Figure 7: SEM image of 304 SS exposed to 1 M HCl solution containing 1.28 mmol/L FPTU

THERMODYNAMIC PARAMETERS OF CORROSION

The activation energy (E_a) for the corrosion process is determined using the equation given below [21]:

$$\ln (r_2 / r_1) = -E_a \, \Delta T / (R \times T_2 \times T_1) \quad (4)$$

Where, r_1 and r_2 are the corrosion rates at temperature T_1 and T_2 and ΔT is the difference in temperature, R is the universal gas constant in Joules. From the Table 4, it is observed that E_a values in the inhibited solution is more than that of the blank/ uninhibited solution, indicating that that the compound FPTU is also effective in reducing the rate of corrosion reactions at lower temperatures [22]. It is also observed from the Table 4 that value of E_a in inhibited solution is less than 80 kJ/mol, confirms that FPTU is physically adsorbed on 304 SS surface [23].The equilibrium constant (K) and the free energy of adsorption (ΔG_{ads}) at different temperatures are calculated using the following equations [24]:

$$K = \theta / C \, (1-\theta) \qquad\qquad (5)$$

Where, θ is the degree of surface coverage on the metal surface, C is the concentration of the inhibitor in mol L^{-1}.

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

Where, R is the universal gas constant in J/k/mol, T is the temperature in Kelvin and 55.5 is the concentration of water in mol L^{-1}.

Generally, higher value of K implies more efficient adsorption

and hence better inhibition efficiency [24]. In the present work, the compound studied has given high values of K, and thus, exhibit higher inhibition efficiencies.

Table 4: Thermodynamic parameters the corrosion of 304 SS in optimal concentration (1.28 mmol/L) of FPTU in 1M HCl

System	$-\Delta G_{ads}$ (KJ/mol)				E_a (kJ/mol)	K
	30ºC	40ºC	50ºC	60ºC		
1M HCl	-	-	-	-	39.75	10332
FPTU	33.46	34.68	35.54	36.52	42.78	

The ΔG_{ads} values for different temperatures are presented in the Table 4. It is apparent from the Table 4 that values of ΔG_{ads} calculated for different temperatures are negative. This indicating the spontaneous adsorption and strong interactions of inhibitor molecules with 304 SS surface [25]. It is also apparent from the Table 4 that ΔG_{ads} values of adsorption are less than -40kJ/mol. This also confirms that FPTU is physically adsorbed on the steel surface [26].

ADSORPTION ISOTHERM

Organic molecules adsorbed on the metal surface plays a key role in controlling the   corrosion of metals and alloys. The Temkin adsorption isotherm model is generally used by a large number of researchers to study the adsorption behavior of organic inhibitors by presuming that organic compounds adsorbed on the metallic surface decreases the surface area accessible for corrosion reactions. The degree of surface coverage (θ) values derived for different temperatures and concentrations of FPTU are examined graphically by fitting to various isotherms. The plot of θ vs. log C demonstrates a linear relationship (Fig. 8) for different temperatures, signifying that the adsorption of the compound FPTU on the surface of 304 SS follows the Temkins adsorption isotherm. The applicability of the Temkin adsorption isotherm verifies the assumption of monolayer adsorption on a uniform homogeneous metal surface. Monolayer adsorption is resulted in the reduction in the surface area accessible for electrochemical reactions [27].
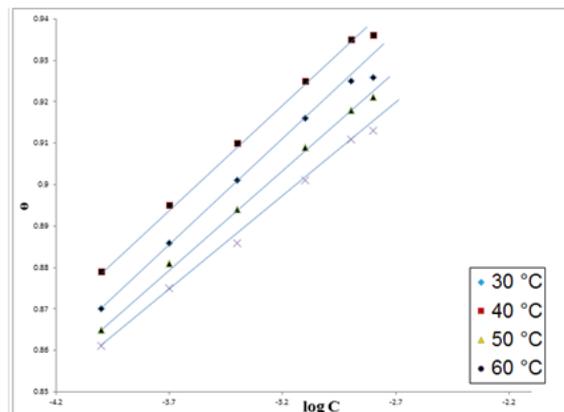

Figure 8: Temkin adsorption isotherm plot for 304 SS

CONCLUSIONS

1. 304 SS shows substantial corrosion in HCl medium due to the presence of chloride ions and the corrosion rate has a linear relationship with the temperatures studied.

2. Corrosion of 304 SS decreases drastically in the presence of inhibitor in HCl medium and the compound inhibit the corrosion of 304 SS both by adsorption and film formation mechanism.

3. The results show that FPTU acts as a mixed inhibitor for the corrosion steel in HCl medium and the addition of this compound shifts the polarization curves to lesser current density values.

4. IE of the compound studied increases with increase in inhibitor concentration up to a critical concentration and decreases marginally with further increase in inhibitor concentration.

5. The compound FPTU has shown maximum inhibition efficiency of greater than 92% at its optimal concentration in all temperatures studied, and hence, it can be efficiently used for commercial application as inhibitor for stainless steel corrosion.

6. The adsorption of the compound on the surface of 304 SS in HCl medium obeys Temkin adsorption isotherm and the thermodynamic results indicate the possibility of physical adsorption of FPTU on 304 SS surface.

7. The study shows that the results obtained from Tafel extrapolation and electrochemical impedance spectroscopy methods are in good agreement.

ACKNOWLEDGEMENT

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