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Investigating the Inhibiting Action of Thiourea Derivative on Mild Steel Corrosion in Acid Medium

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Abstract

The corrosion is a natural phenomenon which affects the productivity and safety of men and machines. Since the mild steel has wide application in almost all industries, and is more prone to corrosion, particularly in acid medium, the present work aims to study the corrosive behavior of mild steel in 0.1N H_2SO_4 medium at different concentrations of N - benzyl - N^1 - phenyl thiourea (BPTU) and temperatures using Tafel extrapolation and linear polarization methods. The results obtained reveal that BPTU is functioning as an excellent anodic inhibitor for mild steel in 0.1N H_2SO_4 medium. The study shows that BPTU adsorbed on the steel surface follows Temkin's adsorption isotherm and the inhibition is governed by physisorption mechanism followed by chemical adsorption. The study also shows that there is a direct correlation between the inhibition efficiency and the temperature studied. The thermodynamic parameters deduced indicated that there is a good interaction between the inhibitor molecules and mild steel surface. The investigation shows that the results obtained from the Tafel extrapolation technique and the linear polarization method are in good agreement. It is evident from the investigation that the compound BPTU can be efficiently used as corrosion inhibitor for mild steel in sulfuric acid solution at the elevated temperatures.

Keywords: corrosion; inhibition; adsorption; polarization; activation energy; mild steel

INTRODUCTION

Corrosion problems are found in all most all the manufacturing sectors resulting in loss of productivity and human life. There are several methods used in industries for mitigating corrosion are proper selection material, coating, use of corrosion inhibitors, and cathodic and anodic protection [1]. Among these, use of inhibitors in the corrosive medium is a simplest, cheapest and trouble-free coating approach to prevent metallic corrosion [2]. Inhibitors are the substances that added in small amount to the acid media, reduces the corrosion reaction rates in metals with medium [3].

Mild steel is a well-known material of construction, which is extensively used in various industries such as chemical processing, transportation, mining, pipe lines etc., and it frequently comes in contact with acid media [4]. The inhibitors used in acid medium during acid pickling and descaling process, get absorbed on the surface of the metallic materials in form of a thin film which decreases the electrochemical reactions [5]. Organic compounds with both N and S atoms and having multiple bonds in their molecules are always gives better performance than the compounds containing N or S alone. Amongst these, thiourea and its derivatives have been widely used as inhibitors in acidic environment for improving the corrosion resistance of different metals and alloys [6-9].

Since mild steel has extensive applications in the different manufacturing sectors including mining industries, and it is more susceptible to corrosion, especially in acid environment, the authors aim to synthesize N - benzyl - N/ - phenyl thiourea for investigating the inhibiting action of this compound for mild steel corrosion in 0.1N H_2SO_4 solution using Tafel extrapolation and linear polarization methods. The schematic representation of Tafel and Linear plots is given the Fig. 1 and 2 respectively [10]. The selection of the compound BPTU is due the reason that thiourea derivatives greatly help to improve the corrosion resistance of metals in acid medium; furthermore, the process of preparation of BPTU is also very simple and cost effective.

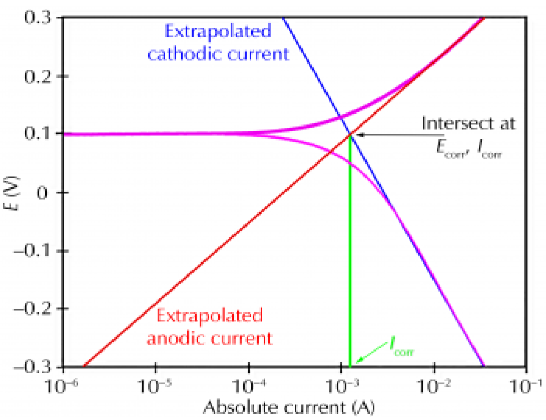

Figure 1: Schematic representation of Tafel plot

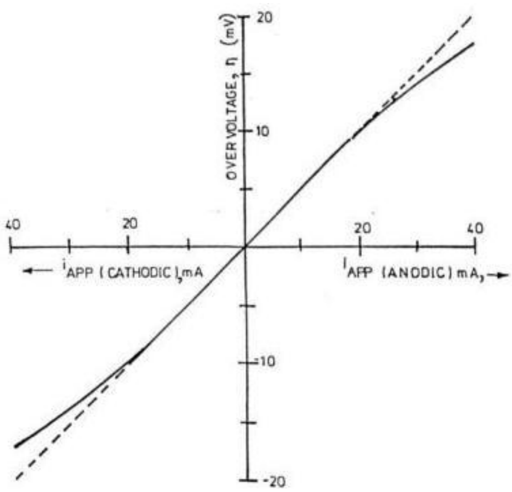

Figure 1: Schematic representation linear polarization curve

EXPERIMENTAL

Specimen and inhibitor preparation

The test specimen with exposed area 0.786 cm^2 and chemical composition (wt%): C: 0.205; Si: 0.06; Mn: 0.55; S: 0.047; P: 0.039 and balance Fe is used in this study. The sample is mirror polished using emery papers, cleaned with distilled water, rinsed in alcohol and then dried in air. AR grade H_2SO_4 and double distilled water are used for preparing the working medium. The compound BPTU ($C_6H_5CH_2NHC(S)NHC_6H_5$) is synthesized by referring the reported procedure of synthesizing the similar compounds [11]. The compound is purified by ethanol and its purity is checked by elemental analysis, and melting point (158°C). The structural formula and elemental analyses are shown in Fig. 3 and Table 1 respectively.

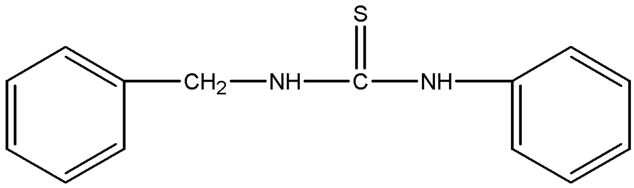

Fig. 3 Structure of the compound BPTU

Table 1: Elemental analysis of BPTU

Inhibitor	Molecular formula	Calculated (Found)%				
		C	H	N	O	S
BPTU	$C_{14}H_{14}N_2S$	69.39 (69.26)	5.82 (5.79)	11.56 (11.60)	-	13.23 (13.19)

Tafel extrapolation technique

The experimental set up used for the polarization studies is shown in Fig. 4. After recording the steady state rest potential (RP) by keeping the circuit open, Tafel experiments are conducted at 28^{0}C from ±250 mV versus RP in step of 20 mV/min., from more negative potential side and the corrosion currents (I) are noted. The experiments are yet again conducted for 40 ^{0}C and 50 ^{0}C. The plot of potential Vs log I, is drawn for calculating corrosion current density (I_{corr}) and corrosion potential (E_{corr}).

Figure 4: Experimental setup

The corrosion rate (CR), the degree of surface coverage (θ) and the percentage inhibition efficiency (% IE) are estimated using equations 1-3. The accuracy of the Tafel results is also verified with linear polarization method.

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

where, i_{corr} is the current density in µA/cm^2, D is the specimen density in g/cm^3, Eq. Wt is the equivalent weight of the specimen in grams (taken as 27.925 grams).

$$\theta = \left[\frac{\left(i_{corr} - i_{corr(inh)}\right)}{i_{corr}} \right] \quad (2)$$

where, $i_{corr(inh)}$ and i_{corr} are the current densities with and without inhibitor respectively.

$$\%IE = \left[\frac{\left(i_{corr} - i_{corr(inh)}\right)}{i_{corr}} \right] \times 100 \quad (3)$$

Linear polarization method

Linear polarization experiments are conducted with ±20 mV Vs OCP in step of 5mV / min from the cathodic side and the corrosion currents (I) were noted. The plots of E versus I are drawn and the slopes of E versus I curves are used for calculating i_{corr} and corrosion rate (CR) as follows in b equations 4 and 1.

$$i_{corr} = 0.026/\text{slope} \quad (4)$$

RESULTS AND DISCUSSION

Effect of inhibitor on mild steel corrosion

The experimental results obtained from Tafel extrapolation technique for mild steel corrosion in 0.1N H_2SO_4 solution, in the absence and presence of BPTU at different solution temperatures are shown in Table 2. The Fig. 5 illustrates the Tafel plot for 100 ppm (maximum concentration) of BPTU on the corrosion of mild steel at 28 ^{0}C in 0.1N H_2SO_4 solution. From the Fig. 5 and Table 2, it is seen that there is a considerable decrease in corrosion rate in the presence inhibitor and a shift in corrosion potential (E_{corr}) in more negative direction. This shift in E_{corr} in the more negative direction in the presence of the compound BPTU, confirms that BPTU is working as an anodic inhibitor for mild steel corrosion in 0.1N sulfuric acid solution. The excellent performance (>90% IE) exhibited by the compound even at a concentration as low as 25 ppm (Table 2) is owing to the existence of protonated form of nitrogen and sulfur atoms of the compound, makes it adsorbed rapidly on the surface of the metal, thus forming an insoluble stable film on the mild steel surface. The experimental results of linear polarization method are shown in the Table 3. From the Table 3, it is observed that there is a good correlation between the Tafel and linear polarization results.

The variation of % IE with increase in inhibitor concentration is shown in Fig. 6. From Fig. 6, it is observed that % IE of the compound has a positive correlation with the concentration of BPTU, except 100 ppm in the range of temperatures studied. This indicates that the optimal concentration required to get maximum IE in all the temperatures is 75 ppm. The decrease in IE in 100 ppm of BPTU may be due to desorption of inhibitor molecules from the steel surface which results in increase in the effective area of attack.

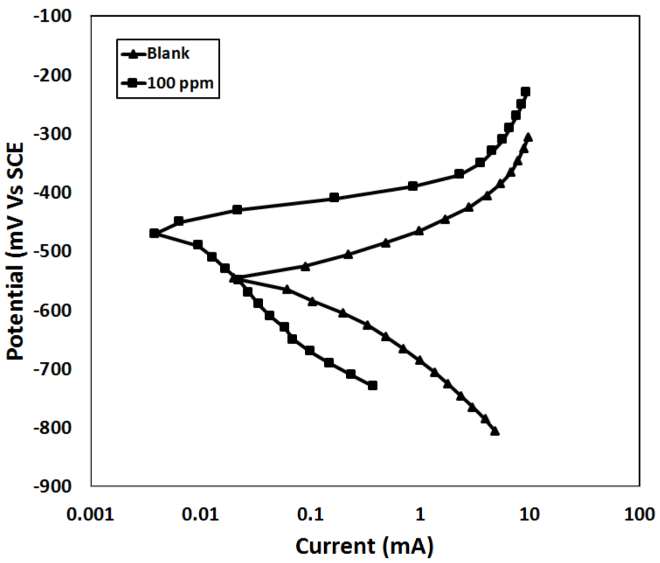

Figure 5: Tafel plot of mild steel in 0.1N H_2SO_4 with and without BPTU at 28 ^{0}C

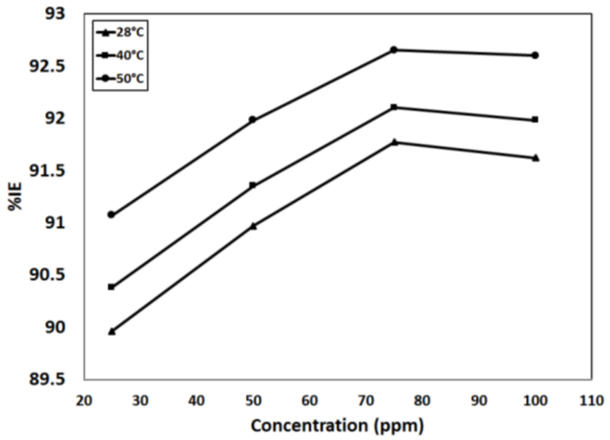

Figure 6: Effect of inhibitor concentration on % IE in 0.1 N H_2SO_4

Table 2: Tafel extrapolation results for mild steel in 0.1N H_2SO_4 with and without BPTU

C (ppm)	28 ^{0}C			40 ^{0}C			50 ^{0}C		
	E_{corr} (mV)	CR (mpy)	IE (%)	E_{corr} (mV)	CR (mpy)	IE (%)	E_{corr} (mV)	CR (mpy)	IE (%)
Blank	-552	61.23	-	-549	86.30	-	-543	157.43	-
25	-522	6.15	89.96	-519	8.30	90.38	-522	14.06	91.07
50	-504	5.53	90.97	-506	7.47	91.35	-515	12.63	91.98
75	-485	5.04	91.77	-495	6.82	92.10	-499	11.57	92.65
100	-476	5.13	91.62	-490	6.92	91.98	-495	11.65	92.60

Table 3: Linear polarization results for mild steel in 0.1N H_2SO_4 with and without BPTU

C (ppm)	28 ^{0}C			40 ^{0}C			50 ^{0}C		
	E_{corr} (mV)	CR (mpy)	IE (%)	E_{corr} (mV)	CR (mpy)	IE (%)	E_{corr} (mV)	CR (mpy)	IE (%)
Blank	-552	61.23	-	-549	86.30	-	-543	157.43	-
25	-522	6.15	89.96	-519	8.30	90.38	-522	14.06	91.07
50	-504	5.53	90.97	-506	7.47	91.35	-515	12.63	91.98
75	-485	5.04	91.77	-495	6.82	92.10	-499	11.57	92.65
100	-476	5.13	91.62	-490	6.92	91.98	-495	11.65	92.60

Effect of solution temperatures on % IE

Fig. 7 illustrates the effect of temperatures on %IE of the compound BPTU. From Fig. 7, it is seen that there is a positive relationship between the %IE of the compound and the solution temperatures.

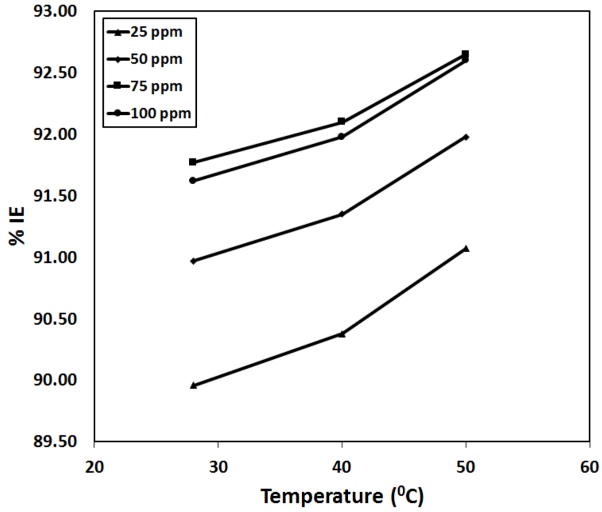

Figure 7: Effect of temperatures on %IE of BPTU

This indicates that the blanketing effect of BPTU is more in elevated temperature as compared to lower temperature which reduces the anodic dissolution of the metal. Therefore, the compound investigated can be efficiently used as inhibitor for mild steel corrosion in 0.1N H_2SO_4 solution in the elevated temperatures. The maximum performance (> 92%) shown by the compound BPTU may be due to its adsorption on the steel surface through polar groups as well as through π-electrons of the double bond.

Inhibition mechanism

To know the mechanism of inhibition, it is necessary to identify the adsorption behavior of the organic compounds on the metal surface. Fig. 8 illustrates Temkin's adsorption isotherm plot for mild steel in 0.1 N H_2SO_4 for different temperatures. From Fig. 8, it is seen that the surface coverage (θ) has a positive correlation with log C, demonstrating that the adsorption of BPTU on the steel surface follows Temkin's adsorption isotherm and its applicability verifies the assumption of mono-layer adsorption on a uniform homogenous metal surface [12].

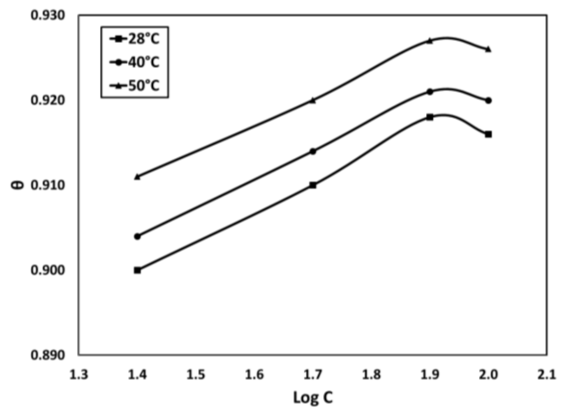

Figure 8: Temkin's adsorption isotherm plot for mild steel at different temperatures in 0.1 N H_2SO_4

Kinetic parameters of adsorption

The free energy of adsorption (ΔG_{ads}) and the equilibrium constant (K) are determined with help of following equations [13],

$$\Delta G_{ads} = -RT \ln (55.5K) \quad (5)$$

where, R is the universal gas constant in J/K/mol and 55.5 is the concentration of water in mols L^{-1}

$$K = \theta / C (1-\theta) \quad (6)$$

where, C is the concentration of BPTU in mol L^{-1}.

The negative values of ΔG_{ads} shown in Table 4, indicated that the compound BPTU gets adsorbed spontaneously on the steel surface [14.15]. The ΔG_{ads} values of BPTU at higher temperature are very nearer to 40 kJ mol^{-1}, signifying that the compound investigated may be physically adsorbed on the steel surface followed by chemical adsorption [16]. The values of activation energy (E_a) are determined by means of the Arrhenius equation [17],

$$\ln (r_2 / r_1) = -E_a \Delta T / (R \times T_2 \times T_1) \quad (7)$$

where, r_1 and r_2 are corrosion rates at temperature T_1 and T_2 respectively and ΔT is the difference in temperature ($T_1 - T_2$). It is observed from the Table 4 that E_a value in the absence of BPTU is more than that of inhibited system. This confirms that the compound BPTU is more effective in elevated temperature [18].

Table 4: E_a and ΔG_{ads} for mild steel

C (ppm)	E_a ($kJmol^{-1}$)	$-\Delta G_{ads}$ ($kJmol^{-1}$)		
		28 °C	40 °C	50 °C
0.1 N H_2SO_4	29.48	--	--	--
100	25.39	35.49	37.06	38.40

CONCLUSIONS

1. The polarization study shows that BPTU is proved to be an excellent anodic inhibitor for mild steel in 0.1N H_2SO_4 medium.
2. The adsorption of BPTU on the mild steel surface follows Temkin's model and the inhibition is governed by physisorption mechanism followed by chemical adsorption.
3. The study demonstrated that BPTU is highly efficient in the elevated temperature.
4. The study shows that corrosion rate increased remarkably with increase in temperature in the uninhibited system.
5. The study also shows the spontaneous adsorption of BPTU on the surface of the mild steel.

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