

A Case Study :

A study on the inhibition of aluminium alloy's corrosion by thiourea derivatives in organic acid

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ABSTRACT

The effects of diphenyl thiourea, phenyl thiourea and N,N'-diethyl thiourea on the corrosion of 1060 aluminium in varying concentration of (0.1N and 0.5N) trichloroacetic acid at 30°C are investigated by weight loss method in conjunction to the concentration of corroding media, period of immersion of Aluminium alloy grade 1060 at the temperature 30°C with respect to the concentration of inhibitor and activation energy and adsorption isotherms are plotted to elucidate the mechanism of adsorption of inhibitor on surface of alloy in that support corrosion potential and polarization behaviour is also observed.

KEY WORDS : Aluminium alloy 1060, Tri-chloroacetic acid, Weight loss, Diphenyl thiourea, Phenyl thiourea, Adsorption, Activation energy

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The carboxylic acid and its chloro derivatives are used in various applications and it has been observed that in the production of these acids or in the other chemical synthesis where chloro-substituted carboxylic acids are used, no metal withstands corrosion [1, 2]. Thiourea has been investigated as corrosion inhibitor extensively and organic compounds that containing both nitrogen and sulphur are reported to have excellent inhibition compared with other compound that containing only nitrogen or sulphur [3-5]. The use of thiourea as corrosion inhibitor for the aluminium alloys in organic acid is not much acknowledged. [6-13]

The present investigation deals with the use of thiourea and its derivatives as inhibitors in Trichloroacetic acid corroding media. For the purpose, aluminium alloy 1060 has been used. The experiments follows varying parameters of inhibitor concentrations (50, 100, 200 and 300 ppm) and also at two concentrations of Trichloroacetic acid (0.1 N and 0.5 N) at 30°C. The exposure period was kept constant for 24 hours.

Percentage inhibition efficiency calculated as

$$E = \frac{W_u - W_i}{W_u} \times 100$$

where:

W_i = Weight loss in inhibited solution

W_u = Weight loss in uninhibited solution

The values of the energy of activation (E_a) and heat of adsorption (Q_{ads}) were given in Table 4. These values were calculated from datas of Table 3 using the following equation:

$$\text{Log} \frac{P_2}{P_1} = \frac{E_a}{2.303R} \left\{ \frac{1}{T_2} - \frac{1}{T_1} \right\}$$

Where, P_1 and P_2 are the corrosion rates mg.dm^{-2} per 6-hour at temperatures T_1 , and T_2 in K, respectively.

The Q_{ads} values were calculated using the equation:

$$Q_{ads} = 2.303 \times R \left(\log \frac{\theta_2(1-\theta_1)}{\theta_1(1-\theta_2)} \right) \times \left(\frac{T_1 \times T_2}{T_2 - T_1} \right)$$

where Q_{ads} = heat of adsorption.

R= Gas constant=1.987kcal mol⁻¹ θ_1 = inhibition efficiency at a temperature T_1 . θ_2 =inhibition efficiency at a temperature T_2 .

Results were summarized in Table 1, 2 and 3 and

Table 1 : Weight loss in (mg) in presence of varying concentrations of inhibitors in 0.1N Trichloroacetic acid and 0.5N Trichloroacetic acid at 30°C for 1060

Concentration	0.1 N Trichloroacetic acid				0.5 N Trichloroacetic acid			
	Wt. loss (mg)	Efficiency	Surface coverage(θ)	Rate (mg/cm ² /hr)	Wt. loss (mg)	Efficiency	Surface coverage(θ)	Rate (mg/cm ² /hr)
	Uninhibited: 770				Uninhibited: 770			
Di phenyl thiourea								
50	131.52	26.53	0.27	0.07	670.3	12.9	0.1	0.4
100	127.45	28.80	0.29	0.07	556.8	27.7	0.3	0.3
200	110.2	38.44	0.38	0.06	534.02	30.6	0.3	0.3
300	128.67	28.12	0.28	0.07	534.18	30.6	0.3	0.3
Phenyl thiourea								
50	133.52	25.41	0.25	0.07	632.24	17.9	0.2	0.3
100	128.45	28.24	0.28	0.07	586.34	23.9	0.2	0.3
200	116.2	35.08	0.35	0.06	564.42	26.7	0.3	0.3
300	126.67	29.23	0.29	0.07	549.2	28.7	0.3	0.3
N,N'-diethyl thiourea								
50	132.46	26.00	0.26	0.07	792.33	-2.9	0.0	0.4
100	128.78	28.06	0.28	0.07	792.31	-2.9	0.0	0.4
200	115.63	35.40	0.35	0.06	792.28	-2.9	0.0	0.4
300	107.39	40.01	0.40	0.06	739.18	4.0	0.0	0.4

Table 2 : Percentage inhibition efficiency of the inhibitors in 0.1N and 0.5N trichloroacetic acid at 30°C inhibitor concentration 50 ppm

Inhibitors	Efficiency (E)					
	0.1N Trichloroacetic acid			0.5N Trichloroacetic acid		
	24 hrs	48 hrs.	72 hrs.	24 hrs.	48 hrs.	72 hrs.
Phenyl thiourea	24.0	48	46	0.2	16	10
Diphenyl thiourea	27.0	45	37	0.1	9	14
N,N'-diethyl thiourea	26.0	46	42	0.0	-2	-4

Table 3 : Percentage inhibition efficiency (E), Energy of activation (E_a), Heat of adsorption (Q_{ads}) and free energy (ΔG) for 1060 alloy in 0.1N Trichloroacetic acid

Inhibitors and concentrations (ppm)	Efficiency (E%)		E _a KJ/mole	Q _{ads} KJ/mole	Free energy KJ/mole	
	30°C	40°C			30°C	40°C
	Di-phenyl thiourea					
50	26.53	56.79	-18.26	51	-17.21	-21.14
100	28.8	53.78	-9.3	42	-15.75	-19.02
200	38.44	56.19	-1.19	29	-15.1	-17.47
300	28.12	55.99	-13.59	47	-12.9	-16.4
Phenyl thiourea						
50	25.41	53.5	-11.93	48	-16.05	-19.74
100	28.24	51.73	-6.35	40	-14.66	-17.75
200	35.08	49.54	3.99	24	-13.72	-15.72
300	29.23	47.98	-0.22	32	-12.02	-14.5
N,N'-diethyl thiourea						
50	26	54.16	-12.96	48	-15.77	-19.44
100	28.06	60.39	-22.95	54	-14.28	-18.31
200	35.4	66.29	-26.74	51	-13.4	-17.16
300	40.01	70.79	-32.08	51	-12.87	-16.65

Fig. 1-4. The inhibition effects di-phenyl thiourea, phenyl thiourea, and N,N'-diethyl thiourea have been investigated at different concentrations at 30°C.

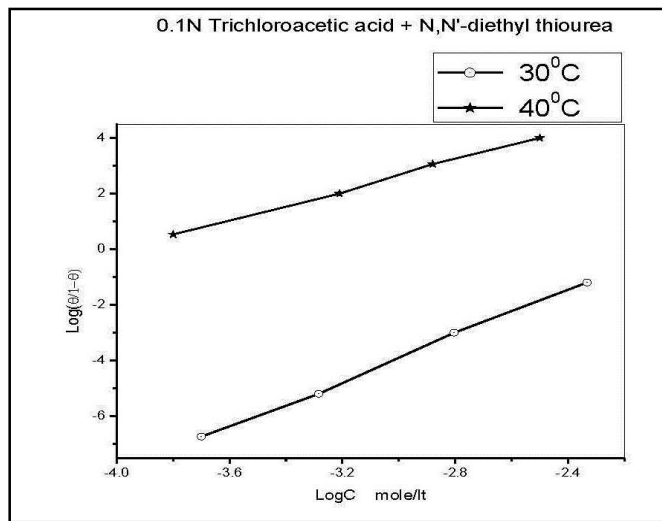


Fig. 1 : Langmuir adsorption plots for 1060 alloy in 0.1N trichloroacetic acid in the presence of N,N'-diethyl thiourea

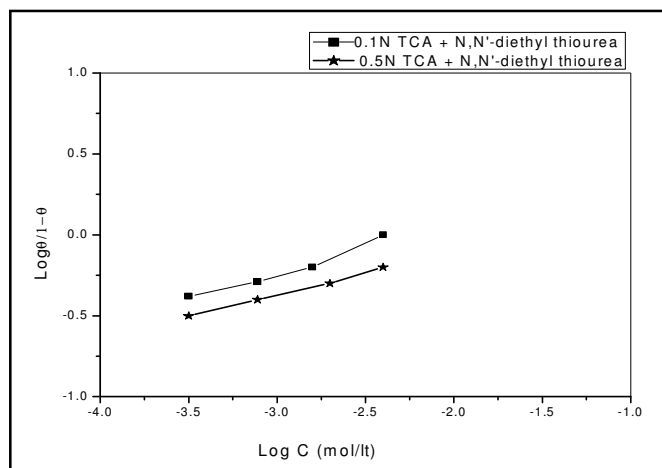


Fig. 2 : Langmuir adsorption plots for 1060 alloy in 0.1N and 0.5N trichloroacetic acid in the presence of N,N'-diethyl thiourea

Table 1 includes the percentage of inhibition efficiencies, surface coverage and rate of corrosion exhibited by the compounds of at 30°C up to the concentration of 300 ppm of inhibitors at an exposure period of 24 hours in 0.1N and 0.5N trichloro acetic acid. It was observed from the table that the percentage inhibition of the inhibitors in case of 0.1N concentration is decreasing with the concentration in all the cases except N,N'-di-ethyl thiourea where increasing behaviour with concentration of the inhibitors has been observed.

In the present system the inhibitive effect of the

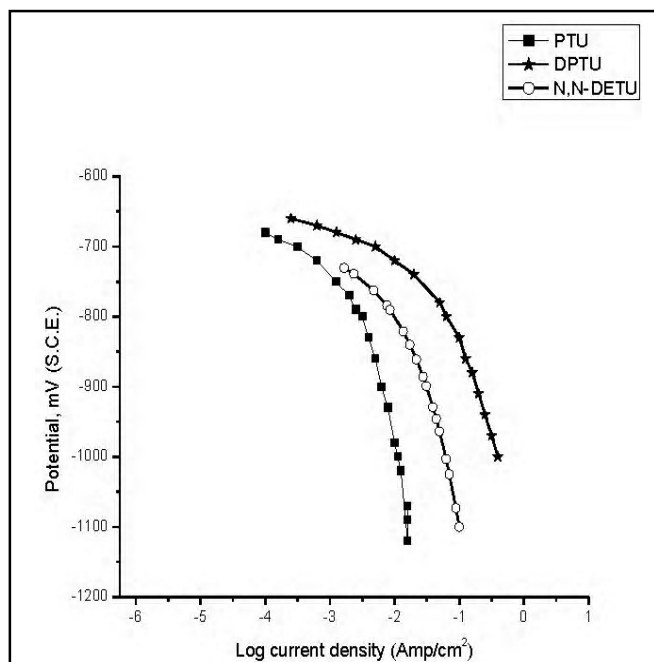


Fig. 3 : Cathodic polarisation curve of 1060 alloy in 0.1N trichloroacetic acid in the presence of inhibitors at 30°C in 0.1N trichloroacetic acid

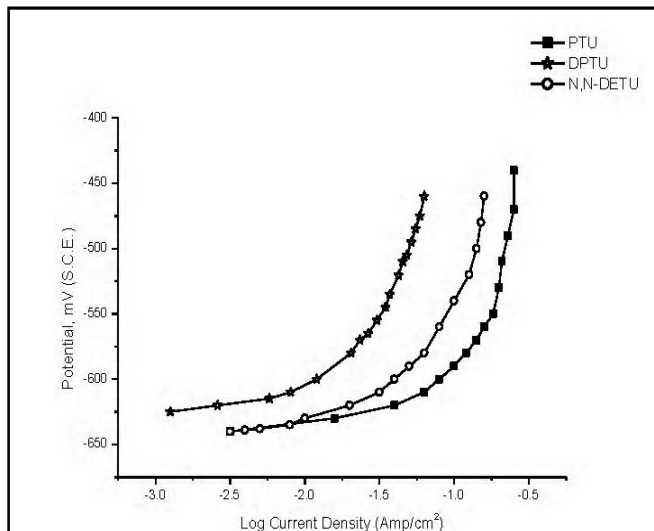


Fig. 4 : Anodic polarisation curve of 1060 alloy in 0.1N trichloroacetic acid in the presence of inhibitors at 30°C in 0.1N trichloroacetic acid

compounds at 30°C have been observed in the following sequence:

Phenyl thiourea < Di-phenyl thiourea < N,N'-diethyl thiourea

The data brings out the fact that when the concentration was increased, di-phenyl thiourea and N, N'-diethyl thiourea, show increase in the inhibition tendency with the rise of concentration of the compounds. The inhibitive effects of the compounds at 30°C have

been observed in the order given below:

N, N'-di-ethyl thiourea < Di-phenyl thiourea < Phenyl thiourea.

In thiourea compounds nitrogen and sulphur are the active centers. These atoms are therefore responsible for the adsorption of thiourea compounds on the metallic surface. Due to adsorption they may block the active sites of the metal and hence may decrease the corrosion rate. Thioureas undergo the process of adsorption that is polarizable. Unbalancing an inhibitor molecule is an effective means for the improvement of its inhibition efficiency [14].

It may also be seen from Table 1 that the effectiveness of the compounds increases with the increase in the temperature from 30°C.

Table 2 shows the effect of the exposure period on the inhibition efficiency of the molecule in 0.1 N and 0.5N Trichloroacetic acid at 30°C. It is clear from the Table 2 that all molecules gives better protection for 48 hours exposure period and after this decrease in inhibition efficiency of the molecule is observed. It is further seen from the Table that the extent of increase in the inhibition efficiency for 0.1N Trichloroacetic acid is more than the extent of decrease, whereas a reverse order has been obtained in 0.5N Trichloroacetic acid.

From the Table 3 it was observed that E_a values of inhibited systems are lower and in some case it is observed negative. A low activation energy means a fast reaction and a high activation energy means a slow reaction[15]. High activation energy corresponds to a reaction rate that is very sensitive to temperature. Conversely small activation energy indicates a reaction rate that varies only slightly with temperature[16]. In some cases activation energy (E_a) are found negative which indicates that the rate decreases with temperature is raised such behaviour is a signal that the reaction has a complex mechanism.

In order to confirm the inhibitors tendency towards the adsorption isotherm, the degree of the surface covered by them was put in the Langmuir's adsorption isotherms[14,17-19]. A plot of $\log \theta/(1-\theta)$ versus $\log C$ is a straight line supporting the monolayer adsorption of the inhibitor. Fig. 1 and 2 shows the linearity in the plots for phenyl thiourea and N, N-di ethyl thiourea in 0.5 N and 0.1N trichloroacetic acid solution, respectively, that shows that compounds are adsorbed on the metal surface and reduce the corrosion rate. This tendency to decrease corrosion rate may be due to the formation of ionisable salts with acid. [20]

Many earlier workers have reported corrosion acceleration in the presence of higher concentrations of

thiourea for other systems[21]. This behaviour was not observed in the case of N, N-di ethyl thiourea and phenyl thiourea in 0.1N and 0.5N trichloroacetic acid.

Polarisation studies:

The cathodic and the anodic polarization studies have been carried out in the presence of the concentrations of the inhibitors for which the observed efficiency was highest at 30°C. The respective plots were shown in Fig. 3 and 4 in 0.1 N and same trend of polarisation was shown by 0.5N Trichloroacetic acid.

Following are the observations drawn from the figures:

The cathodic polarization curves in the presence of the inhibitors were almost similar to the curves in their absence[22]. The cathodic lines in the presence of these compounds have shifted towards active direction corresponding to their steady state potentials. The anodic polarization curves in the presence of the inhibitors have shifted towards left *i.e.* in lower current density side.

Di-phenyl thiourea and N, N'-di ethyl thiourea were equally effective on cathode as well as anode.

The parallel cathodic polarization lines show that the inhibitors do not interfere with the cathodic reaction taking place on the metal surface. The inhibitors have shifted the steady state potential in the active direction. These results indicate that the inhibitors simply block the cathodic reaction sites on the metal surface. This simple blocking effect decreases the number of the surface metal atoms at which corrosion reactions may take place smoothly in the absence of the inhibitors, and hence decrease in the corrosion rate was observed

Conclusion:

The corrosion rate of 1060 aluminium increases with an increase in concentration of acid. It has been observed that the inhibition efficiency of the inhibitors showed increasing tendency with increase in temperature. Better inhibition was given by all compounds for 48 hours exposure period.

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