Thiourea Derivatives as Inhibitors for the Corrosion of Mild Steel in Hydrochloric Acid

M. N. DESAI AND M. B. DESAI

Chem. Dept., Univ. School of Sciences, Gujarat University, Ahmedabad-380 009

THIOUREA has been investigated as corrosion inhibitor for metals in acidic media, but substituted thiourea derivative have received lesser attention so far. The present article reports results obtained in the investigations on the use of phenylthiourea, diphenylthiourea, o-tolylthiourea and p-tolylthiourea as inhibitors for the corrosion of mild steel in hydrochloric acid solutions. The influence of parameters like inhibitor concentration, time, hydrocholoric acid concentration has been investigated. The mechanism of inhibitor action has been studied by the galvanostatic method. The preparation of specimens and corrosion tests were carried out as described in our earlier publication[1].

Observations : The corrosion of mild steel in hydrochloric acid solutions increases with time as well as with hydrochloric acid concentration. Polarisation measurements in 1.0 N and 6.0 N HCl indicate that the corrosion process is cathodically controlled.

The influence of time and hydrochloric acid concentration on the performance of inhibition is given in table 1 and the influence of inhibitor concentration is shown in table 2. The influence of current density on the cathode and anode potentials of mild steel in 1.0 N HCl and 6.0 N HCl in the presence and absence of inhibitors is given in figures 1 and 2 respectively.

Phenylthiourea : At 0.01% concentration phenylthiourea gives a satisfactory protection to mild steel in hydrochloric acid and a ten fold increase in inhibitor concentration increases its protectivity to 90% or more (Table 2). Its efficiency improves with an increase in HCl concentration. The efficiency of phenylthiourea shows significant improvement with the passage of time (Table 1), and with hydrochloric acid concentration (Table 1).

In 1.0 N hydrochloric acid addition of 0.01% phenylthiourea shifts the corrosion potential in the positive direction by 40 mV and at 0.1% concentration this shift is +60 mV. In 6.0 N hydrochloric acid, the addition of phenylthicurea shifts the corrosion potential in the negativs direction by 10 mV. At both the concentration of hydrochloric acid, phenylthiourea is a cathodic inhibitor (Figures 1 and 2).

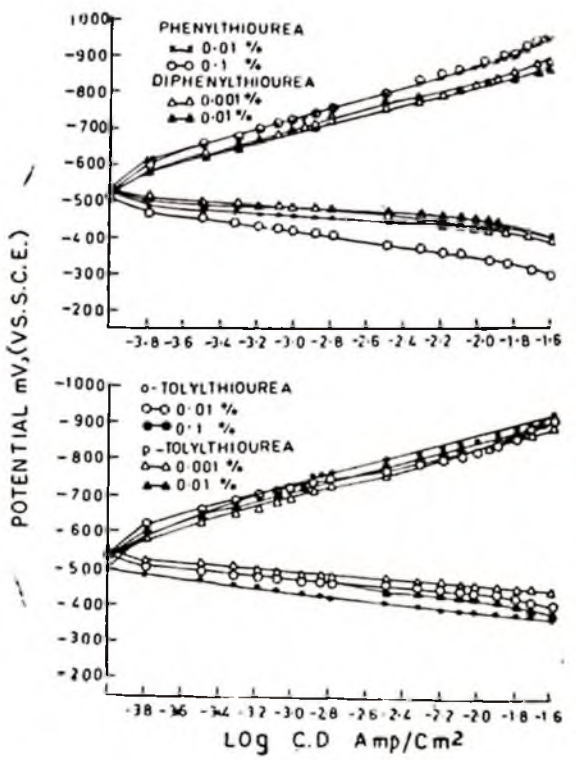


Fig. 1. Influence of current density on cathode and anode potentials of mild steel in 1.0 N hydrochloric acid solution in presence and absence of inhibitors.

Diphenylthiourea : Even at 0.001% concentration diphenylthiourea gives more than 60% protection to mild steel in HCl solutions and a tenfold increase in inhibitor concentration, raise the protectivity to 81–88% (Table 2). Its efficiency remains constant with time in 1 N to 4 N (Table 1). In 1.0 to 4.0 N solutions of hydrochloric acid, in general, the protective action of diphenylthiourea improves with the passage of time (Table 1).

Addition of diphenylthiourea to 1.0 N hydrochloric acid shifts the corrosion potential in positive direction by 40 mV but in 6.0 N hydrochloric acid the corrosion potential remains unchanged. In 1.0 N

TABLE 1

Effect of time and hydrochloric acid concentration on the corrosion loss (mg/dm²) of mild steel (Values in the brackets show % efficiency)

Temperature : 35°±0.5°C

Inhibitor concentration (%)	Normality of HCl	1 hour	3 hours	6 hours	9 hours	12 hours	24 hours
Nil	1.0	32	72	171	328	592	1229
	2.0	64	134	250	701	1160	1668
	3.0	90	425	900	1439	22.2	4729
	4.0	124	1029	2642	3658	4806	7066
Phenylthiourea 0.1 %	1.0	7 (78)	15 (79)	35 (80)	42 (87)	49 (92)	140 (89)
	2.0	11 (83)	26 (81)	66 (74)	72 (90)	79 (93)	184 (89)
	3.0	16 (83)	47 (89)	105 (88)	135 (91)	158 (93)	355 (92)
	4.0	20 (84)	62 (94)	148 (94)	199 (95)	240 (95)	419 (94)
Diphenylthiourea 0.1 %	1.0	7 (78)	16 (78)	34 (80)	65 (80)	89 (85)	186 (85)
	2.0	11 (83)	28 (79)	55 (78)	140 (80)	141 (88)	316 (81)
	3.0	13 (86)	42 (90)	115 (87)	225 (84)	230 (90)	579 (88)
	4.0	21 (83)	70 (95)	142 (95)	322 (91)	397 (92)	1041 (89)
o-Tolylthiourea 0.1 %	1.0	6 (81)	14 (81)	27 (84)	40 (88)	56 (91)	77 (94)
	2.0	8 (88)	24 (82)	42 (83)	70 (90)	75 (94)	94 (94)
	3.0	14 (84)	40 (91)	69 (92)	108 (92)	172 (92)	196 (96)
	4.0	22 (82)	59 (94)	114 (96)	181 (95)	257 (95)	299 (96)
p-Tolylthiourea 0.01 %	1.0	6 (81)	12 (83)	18 (89)	28 (91)	35 (94)	82 (93)
	2.0	8 (88)	14 (90)	19 (92)	33 (95)	40 (97)	121 (93)
	3.0	11 (88)	22 (95)	40 (96)	46 (97)	51 (98)	264 (94)
	4.0	20 (84)	39 (96)	73 (97)	114 (97)	152 (97)	180 (97)

hydrochloric acid, addition of 0.01% diphenylthiourea induces a significant increase in both the cathode and anode polarisations. In 6.0 N HCl, the increase in cathode polarisation is evident from the current density 1.14×10^{-3} amp/cm^2 (Figures 1 and 2).

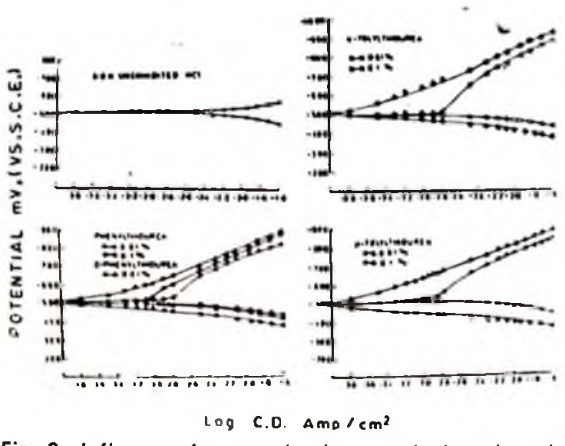


Fig. 2 Influence of current density on cathode and anode potentials of mild steel in 6.0 N hydrochloric acid solution in presence and absense of inhibitors

o-Tolylthiourea : At 0.01% concentration, o-tolylthiourea gives 90-93% protection to mild steel in 1.0 N – 4.0 N HCl and a ten-fold increase in inhibitior concentration brings about a slight improvement in its protectivity (Table 2). In 1.0 N, 2.0 N, 3.0 N solutions of hydrochloric acid, the efficiency of o-tolylthiourea improves with time but in 4.0 N hydrochloric acid it is constant for the durations of the study (Table 1). In general, its efficiency improves with an increase in HCl concentration.

Addition of o-tolylthiourea to 1.0 N hydrochloric acid shifts the corrosion potential in the positive direction and this is more evident with an increase in inhibitor concentration. However, in 6.0 N hydrochloric acid addition of o-tolylthiourea shifts the corrosion potential in the negative direction. At both the concentration of hydrochloric acid, the predominant effect of o-tolylthiourea is on the cathodic reaction (Figures 1 and 2).

p-Tolylthiourea : Even at as low a concentration as 0.005%, p-tolylthiourea gives 86-94% protection to mild steel in 1-4 N HCl, and at 0.02% concentration, the protection afforded is 93-97% (Table 2). In general the efficiency of p-tolylthiourea improves with the passage of time and hydrochloric acid concentration (Table 1).

In 1.0 N hydrochloric acid addition p-tolylthiourea shifts the corrosion potential in the positive direction but in 6.0 N hydrochloric acid this shift is in the negative direction. p-Tolylthiourea is a cathodic inhibitor in 1.0 N HCl as well as in 6.0 N HCl.

TABLE 2

Effect of inhibitor concentration on the corrosion loss (mg/dm^2) of mild steel in hydrochloric acid (Values in the brackets show% efficiency)

Inhibitor and Inhibitor concentration	1.0 N HCl	2.0 N HCl	3.0 N HCl	4.0 N HCl
Nil	1229 (–)	1668 (–)	4729 (–)	7066 (–)
Phenylthiourea				
0.01 %	222 (22)	254 (85)	518 (89)	607 (91)
0.02 %	149 (88)	213 (87)	412 (91)	521 (93)
0.05 %	127 (90)	173 (90)	307 (94)	373 (95)
0.1 %	140 (89)	184 (89)	355 (92)	416 (94)
Diphenylthiourea				
0.001 %	471 (62)	615 (63)	1250 (74)	2152 (70)
0.005 %	213 (83)	324 (81)	789 (83)	1147 (84)
0.01 %	186 (85)	315 (81)	579 (88)	1041 (85)
O – Tolylthiourea				
0.01 %	128 (90)	152 (91)	426 (91)	502 (93)
0.05 %	80 (93)	151 (91)	292 (94)	393 (94)
0.1 %	77 (94)	94 (94)	196 (96)	299 (96)
p-Tolylthiourea				
0.005 %	170 (86)	216 (87)	372 (92)	432 (94)
0.01 %	136 (89)	134 (92)	330 (93)	194 (97)
0.02 %	82 (93)	121 (93)	264 (91)	180 (97)

TABLE 3

Tafel parameters and efficiency of inhibitors in 1.0 N and 6.0 N HCl

Inhibitor and Inhibitor concentration %	TAFEL SLOPE b		Energy transfer coefficient Cathodic	CORROSION CURRENT Amp/cm² ×10⁻³		Inhibitor efficiency (%) from (5)	Inhibitor efficiency (%) from (6)	Inhibitor efficiency from loss in weight method
	Anodic (Volts)	Cathodic (Volts)		From extrapolation of cathodic tafel line	From intersection of cathodic and anodic lines at open circuit potential			
1	2	3	4	5	6	7	8	9
Uninhibited 1.0 N HCl	0.06	0.125	0.48	2.27	2.08	—	—	—
Phenylthiourea 0.1 %	0.06	0.18	0.33	0.06	0.04	97	98	79-92
Diphenylthiourea 0.01 %	0.05	0.12	0.50	0.07	0.07	97	97	79-85
o-Tolylthiourea 0.1 %	0.062	0.15	0.40	0.06	0.033	97	99	81-94
p-Tolylthiourea 0.01 %	0.13	0.13	0.46	0.72	0.031	97	96	81-94
Uninhibited 6.0 N HCl	0.06	0.11	0.55	4.87	3.6	—	—	—
Phenylthiourea 0.1 %	0.07	0.23	0.26	0.1995	0.1995	93	94	97
Diphenylthiourea 0.01 %	0.09	0.23	0.26	0.5012	0.3981	90	89	86
o-Tolylthiourea 0.1 %	0.07	0.23	0.26	0.1585	0.1905	97	95	98
p-Tolylthiourea 0.1 %	0.06	0.19	0.32	0.1624	0.1624	97	95	98

Mode of Adsorption : Plots of log surface coverage against log inhibitor concentration show that Freundlich adsorption isotherm is obeyed in the effective concentration range.

Polarisation data : The tafel slopes and inhibitor efficiencies calculated from polarisation curves in 1.3 N HCl and 6.0 N HCl are given in table 3. In general there is a good correlation between the percentage efficienciencies calculated from polarisation data and loss in weight data. At lower inhibitor concentration, the protectivity is generally lesser than that at higher inhibitor concentration. This tallies well with lower values of tafel slopes obtained at lower inhibitor concentrations.

Influence of temparature : Activation energies of mild steel in inhibited 1.0 N HCl were calculated from Arrhenius plots. It was observed that in uninhibited hydrochloric acid, the activation energy of mild steel is 18.0 kcal per mole. At effective concentration of the inhibitors, the activation energy of mild steel was found to be :

	Concentration	Activation energy k cal/mole
Nil		18.8
Diphenylthiourea	0.01%	19.9
Phenylthiourea	0.1 %	14.6
o-tolylthiourea	0.1 %	7.0
p-tolylthioutea	0.01%	16.7

Thus the protectivity of the last three compounds, improves with an increase in temperature.

Cathodic protection : Studies of cathodic protection of mild steel in 6.0 N HCl in the presence and absence of inhibitors show that cathodic protection experiments is given in table 4. All the compounds reduce the protective current. A comparision of the values of protective current shows that substitution of a hydrogen atom in thiourea by tolyl groups is more favourable by the substitution by phenyl group. o-Substitution gives better inhibition than para substitution.

It is interesting to note that at 0.1% concentration, both o-tolylthiourea and p-tolylthiourea afford 98% protection to mild steel in 6.0 N HCl. However in the persence of o-tolylthiourea the value of protective current is less (0.065 amp/dm^2) than that required in the presence of p-polylthlourea (0.097 amo/dm^2) indicating that under the influence of impressed cathodic current, there is an improvement in the adsorption characteristics of of o-tolylthiourea.

It has been shown by Rajagopalan[2] that with quinoline, (β-naphthol, thiourea and gelatine in the case of mild steel in 5% sulphuric acid the potential corresponding to the protection current is not a constant value and varies with each system (This is in agreement with the present work). They further state that the protective potential remains the same for the same system at all concentrations of the inhibitor though the protection current varies. The

TABLE 4

Weight loss in the absence and presence of protective current, electrode potentials and efficiencies for mild steel in 6.0 N HCl

Inhibitor concentration %	Without external cathodic current			With external cathodic current			
	Weight loss mg/dm^2	Inhibitor efficiency (%)	Open circuit potential in mv. with ref. to S.C.E.	Current for complete protection amp/dm^2	Protective potential in mV with ref. to S.C.E.	Theoretical current needed for complete protection amp/dm^2	Ratio of theoretical current to observed current
Nil	1458	—	-500	1.300	-660	0.453	0.35
Phenylthiourea							
0.01 %	280.0	81	-510	0 324	-640	0.087	0.27
0.1 %	39.0	97	-510	0.130	-640	0.012	0.09
Diphenylthiourea							
0.01 %	202.5	86	-500	0.227	-635	0.063	0.28
o-Tolylthiourea							
0.01 %	190.0	87	-500	0.227	-655	0.059	0.26
0.1 %	35.6	98	-510	0.065	-640	0.011	0.17
p-Tolythiourea							
0.01 %	175.0	88	-505	0.194	-640	0.054	0.28
0.1 %	32 4	98	-505	0.0972	-640	0.01	0.10

present study however reveals that the potentials change with inhibitor concentration.

Protective potentials becoming more positive with an increase in the inhibitor concentration, may indicate that the prefetential effect of these inhibition is on the local cathodes and as the concentration of the inhibitor is increased, the local anodes are also affected.

The difference effect is positive in the presence and absence of inhibitors.

CONCLUSIONS

Thiourea and related compounds have been extensively investigated as corrosion inhibitors in acidic media. The inhibitive action of thiourea and related molecules depends on the presence of N and S atoms in the molecule and therefore such compounds are versatile corrosion inhibitors. In general, tolylthioureas have been found to be better inhibitors than phenylthiourea and diphenylthiourea. Talbot[3] observed that phenylthiourea is an excellent inhibitor for the corrosion of iron in 5 N HCl (24 hours duration) and at 1.0% concentration gives 95-98% protection. Its inhibitive action is enhanced by the addition of small amount of KI. Cavallaro[4] studied various compounds as inhibitors for the corrosion of mild steel in hydrochloric acid and observed that phenylthourea acts as an inhibitor by influencing the cathodic reaction. Makrides[5] studied the effect of thiourea derivatives on the solution rate of mild steel in hydrochloric acid. He observed that diphenylthiourea are adsorbed on the iron surface in 5.0 N HCl.

Cavallaro[6] observed that phenyl and tolylthioureas are good inhibitors for the corrosion of mild steel in 5.0 N hydrochloric acid (2 hours). The relative sequence being p-tolyl > o-tolyl > phenyl. Our observations are in good agreement with the observations of Cavalloro. They act by general adsorption on the metallic surface consequently increasing the hydrogen over-voltage. Cavallaro[7] investigated the S containtng compounds as corrosion inhibitors with a view to investigate the relation between the structure of compound and inhibitive action. He observed that asymetrical thiourea derivatives are better inhibitors which is in agreement with our observations which show that phenylthiourea is a better inhibitor than diphenylthiourea.

REFERENCES

1. M. N. Desai, S. M. Desai. *Second Symposium on Corrosion Inhibitors*, Ferrara, 1966, p. 863.

2. Rajagopalan et al., *J. Electrochem. Soc.* 107 (5), 1960, 379-382.

3. M. Tolbot, *Second Symposium on Corrosion Inhibitors*, Ferrara, (1965) pp. 363-375.

4. L. Cavallaro et al., *Second International Congress on Metallic Corrossion*, Texas (1966), pp. 581-583.

5. A. C. Makrides and N. Hackerman, *Industrial Engineering Chemistry*, (1955), pp. 1773-1781.

6. L. Cavallaro, et al., *First Syposium on inhibitor of Corrosion* Ferrara (1960), pp. 112-135.

7. L. Cavallaro and G. Bolognes, *Atti Acad. Sci.* Ferrara, 24 6 pp. 1946-47.