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Effect of Some Thioureas on the Corrosion of 1100 Aluminium in Acidic Chloride Solution

P.N.S. YADAV* and R.WADHAWANI
Department of Chemistry
K.S. Sakat Post Graduate College
Faizabad 224 001, India

The effect of urea, thiourea and some of its derivatives namely phenyl thiourea, *o*-tolyl thiourea, *m*-tolyl thiourea, *p*-tolyl thiourea, 1:3-di-*o*-tolyl thiourea, 1:3-di-*m*-tolyl thiourea and 1:3-di-*p*-tolyl thiourea on the corrosion of 1100 aluminium has been studied in 1% hydrochloric acid using different concentrations of the compounds at 25°, 35° and 45°C. The inhibition efficiencies of the inhibitors were found to increase with increase in temperature from 25° to 45°C. Better inhibition was given by all compounds for 48 h exposure period.

INTRODUCTION

Thiourea and its derivatives are important organic inhibitors due to their polar character with the sulphur atom having permanent negative charge whereas the nitrogen atom has positive charge. As the molecule approaches the corroding metal surface, the electronic layer of the Helmholtz double layer tends to increase the polarisation of the molecule and induces additional positive charge on both the sulphur and the nitrogen atoms. It is a condition that enhances the absorbability of the molecule on the metallic surface.

Many workers have been using different thiourea compounds as inhibitors for aluminium alloys in different media[1,2] and others have also been using thiourea derivatives for different systems[3–6]. Makwana *et al.*[7] investigated that thiourea, phenyl thiourea and 1:3-di-*o*-tolyl thiourea worked as corrosion inhibitors for aluminium and its alloys in hydrochloric acid. Although thiourea and its compounds are good inhibitors for certain metals in different media but the relation between inhibition efficiency of the compounds and its substituent group is not well established. In the present investigation an attempt has been made to study the inhibitive effect of different thiourea derivatives for 1100 aluminium alloy in 1% and 5% hydrochloric acid solution.

EXPERIMENTAL

Aluminium sheets (1100) were supplied by M/s. Hindalco. Hydrochloric acid, BDH AnalaR grade, was used for the preparation of the solutions. Inhibitors, *viz*.,

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*Kendriya Vidyalaya, Mughalsarai (Varanasi)-232101, India.

phenyl thiourea (PhTU), *o*-tolyl thiourea (*o*-tolTU) *m*-tolyl thiourea (*m*-tolTU), *p*-tolyl thiourea (*p*-tolTU), 1:3-di-*o*-tolyl thiourea (1:3-di-*o*-tolTU), 1:3-di-*m*-tolyl thiourea (1:3-di-*m*-tolTU) and 1:3-di -*p*-tolyl thiourea (1:3-di-*p*-tylTU) used were AR grade or synthesized in the laboratory, recrystallized and purity confirmed by determining sharp melting points. The solutions were prepared in double distilled water. Specimens used for the weight loss experiments were 75 x 50 mm. They were polished successively with 1/0, 2/0, 3/0 and 4/0 grades of wax coated emery paper, followed by cleaning with benzene and soap, and finally with acetone. Then they were stored in a vacuum desiccator. The experiments were performed in 500 ml corning glass beaker (without lid). 300 ml 1% hydrochloric acid solution was taken to submerge the specimen completely at 25°, 35° and 45°C and with 50, 100, 200 and 300 ppm of the inhibitor. The weight losses were determined after dipping the corroded specimens in 70% nitric acid for 5 min, and then washing them thoroughly with distilled water and drying. Three test coupons were used for each corrosion test to find out the average corrosion rate.

Inhibitive efficiencies were calculated with the equation:

$$E = \frac{p - q}{p} \times 100$$

where p = weight loss in uninhibited solution
q = weight loss in inhibited solution
and E = percentage inhibition efficiency.

The inhibition efficiency was taken to represent the surface coverage (θ). The results were shown in the form of Langmuir plots, that is

$$\log \theta/(1 - \theta) \text{ vs } \log c$$

For the polarisation studies the working electrodes were *flag-shaped*, 2 cm^2, with a side tag of length 40 mm. Part of the tag was blocked off with paraffin wax leaving the upper part bare to make electrical contact. The experiments were carried out in a 200 ml pyrex glass cell containing 100 ml test solution (1% hydrochloric acid, without and with concentration of inhibitors at which maximum efficiency was observed at 35°C). Platinized platinum foil was used as the auxiliary electrode. Saturated calomel electrode with Luggin capillary was used for the measurement of electrode potentials. Potentio-static anodic and cathodic polarisation experiments were carried out using a Wenking (laboratory model) potentiostat. The electrode was made either the anode or the cathode and the changes in current were measured after every change of potential starting from a steady state corrosion potential. All experiments were carried out in an air thermostat electronically controlled at 35° ± 0.2°C.

RESULTS AND DISCUSSION

Loss in weight and percentage inhibition efficiency at different concentrations of thiourea and its derivatives in 1% HCl at 25°, 35° and 45° for 24 h exposure period are given in Table 1. It is seen from the Table that the percentage inhibition

TABLE 1
LOSS IN WEIGHT (m, mg), PERCENTAGE INHIBITION EFFICIENCIES (E) AND HEAT OF ADSORPTION (Q_{ads}) OF THE INHIBITORS IN 1% HCl
(Exposure period = 24 h)

Inhibitors and concentrations in ppm	Temperature						Temperature range	
	25°C		35°C		45°C		25°–35°C	35°–45°C
	m	E	m	E	m	E	Q_{ads}, kcal/mole	Q_{ads}, kcal/mole
Uninhibited	58.00	—	96.00	—	207.00	—	—	—
Urea								
50	49.88	14	89.28	7	196.65	5	–14.07	–6.96
100	51.00	12	91.20	5	198.72	4	–17.36	–4.55
200	51.62	11	92.16	4	202.86	2	–19.84	–13.89
300	52.20	10	92.16	4	204.93	1	–17.89	–27.59
Thiourea								
50	42.34	27	68.16	29	134.55	35	18.06	5.37
100	47.56	18	76.80	20	144.90	30	2.38	10.49
200	48.14	17	73.92	23	153.18	26	6.88	3.16
300	49.30	15	75.84	21	157.32	24	7.47	3.35
Phenyl thiourea								
50	41.76	28	67.20	30	124.20	40	1.77	8.61
100	42.88	26	70.08	27	132.48	36	0.94	8.16
200	43.60	25	71.04	26	144.90	30	0.96	3.87
300	43.60	25	71.04	26	149.04	28	0.96	1.98
o-tol TU								
50	45.24	22	72.00	25	134.55	35	3.05	9.33
100	49.40	15	78.72	18	144.09	30	3.98	13.02
200	56.84	2	90.24	6	165.60	20	20.74	26.58
300	58.58	–1	100.00	0	180.09	13	24.76	26.43
m-tol TU								
50	48.14	17	77.76	19	138.69	33	2.47	14.44
100	53.36	8	87.36	9	169.74	18	4.98	15.49
200	56.84	2	94.08	2	190.44	8	0.00	28.21
300	61.48	–6	101.76	–6	202.86	2	0.00	—

Inhibitors and concentrations in ppm	Temperature						Temperature range	
	25°C		35°C		45°C		25°–35°C	35°–45°C
	m	E	m	E	m	E	Q_{ads}, kcal/mole	Q_{ads}, kcal/mole
p-tol TU								
50	44.66	23	72.00	25	130.04	37	2.00	11.03
100	45.82	21	72.96	24	140.76	32	3.14	7.76
200	47.54	18	74.80	22	149.08	28	4.57	6.26
300	48.14	17	75.84	21	155.25	25	4.78	4.41
1 : 3-di-o-tol TU								
50	44.66	23	72.96	24	93.15	55	1.01	26.34
100	43.60	25	70.08	27	95.22	54	1.90	22.49
200	40.02	31	62.36	34	91.00	56	3.31	16.74
300	42.92	26	69.12	28	91.00	56	1.85	23.08
1 : 3-di-m-tolTU								
50	46.40	20	72.00	25	99.36	52	16.30	22.94
100	46.98	19	73.92	23	101.43	51	4.40	24.30
200	47.54	18	74.80	22	82.80	50	4.57	32.53
300	48.72	16	79.68	17	107.64	48	1.32	29.31
1 : 3-di-p-tol TU								
50	48.14	17	73.92	23	95.22	54	6.88	26.64
100	44.08	24	71.04	26	82.80	60	1.95	28.25
200	44.02	31	63.12	33	72.45	65	2.50	24.96
300	37.70	35	60.48	37	62.12	70	1.56	26.85

efficiency decreases with the increase in concentration in all the cases except *o*- and *m*-tolTU. When oxygen atom of urea is substituted by sulphur atom, effectiveness of the compound enhances appreciably. The substitution of a phenyl ring at one of the nitrogen atoms of the TU increases the percentage inhibition efficiency of the compound to some extent. The substitution of $-CH_3$ group at *o*-, *m*-, or *p*-positions of the phenyl ring has no beneficial effect whether monosubstituted or disubstituted. In 1% hydrochloric acid the inhibitive effects of the compounds at 35°C have been observed in the following sequence:

Urea < *m*-tolTU < *o*-tolTU < 1:3-di-*m*-tolTU < *TU* <
1:3-di-*o*-tolTU < *p*-tolTU < 1:3-di-*p*-tolTU < pHTU

Table 2 gives the loss in weight and percentage inhibition efficiency at 35°C

TABLE 2
LOSS IN WEIGHT (m, mg) AND PERCENTAGE INHIBITION EFFICIENCIES (E) OF THE INHIBITORS IN 5% HCl AT 35°C
Exposure period= 24 h

Inhibitors and concentrations in ppm	m	E
Uninhibited	1578	—
Urea		
50	1499.10	5
100	1546.44	2
200	1593.78	–1
300	1625.34	–3
Thiourea		
50	1325.52	16
100	1451.76	8
200	1476.54	7
300	1530.66	3
Phenyl thiourea		
50	1199.28	24
100	1246.62	21
200	1278.18	19
300	1341.30	15
o-tol TU		
50	1562.22	1
100	1593.78	–1
200	1641.12	–4
300	1656.90	–5
m-tol TU		
50	1562.22	1
100	1562.22	1
200	1593.78	–1
300	1641.12	–4
p-tol TU		
50	1215.06	23
100	1357.08	14
200	1499.10	5
300	1514.88	4
1:3-di-o-tol TU		
50	1388.64	12
100	1151.94	27
200	1104.60	30
300	1104.60	30
1:3 -di-m-tol TU		
50	1309.74	17
100	1215.06	23
200	1167.72	26
300	1136.16	28

Inhibitors and concentrations in ppm	m	E
1:3 -di-p-tol TU		
50	1641.12	–4
100	1641.12	–4
200	1641.12	–4
300	1625.34	–3

in the presence of different concentrations of the inhibitors in 5% hydrochloric acid. It is evident from the Table that 1:3-di-*p*-tolTU accelerates the corrosion rate at all the concentrations studied although the extent of acceleration is low. It is further evident from the Table that urea, *o*-tolTU and *m*-tolTU increase the corrosion rate of 1100 aluminium in 5% HCl at their higher concentrations. However, they have very poor inhibition tendency at their lower concentrations. The percentage inhibition efficiencies have been found to decrease with rise in concentration in the presence of all thioureas, but an inverse trend is observed for 1:3-di-*o*-tolTU. It is surprising to note that 1:3-di-*p*-tolTU accelerates corrosion rate of aluminium at all concentrations, whereas inhibitive behaviour is shown by this compound in 1% hydrochloric acid. The percentage inhibition efficiency in 5% HCl at 35°C decreases in the order given as under:

1 : 3-di-*o*-tolTU > 1 : 3-di-*m*-tolTU > PhTU > *p*-tolTU >

TU > Urea > *m*-tolTU > *o*-tolTU > 1:3-di-*p*-tolTU

Generally adsorption of organic compounds on the metal surface takes place *via* sulphur, oxygen and nitrogen atoms and in some cases by selenium and phosphorus. Oxygen, nitrogen and sulphur are the active centre for the process of adsorption in urea and thioureas. Therefore, these atoms are responsible for the absorption of urea and thioureas on the metallic surface. Due to adsorption they may block the active sites of the metal and hence may decrease the corrosion rate. Urea shows a poorer inhibition than thiourea because of the fact that oxygen atom of the urea through which it can undergo the process of adsorption is less polarizable than the sulphur atom of TU which is considered to be the reaction centre for the adsorption of thio compounds if nitrogen atom is present[8]. Imbalancing an inhibitor molecule is an effective means for the improvement of its inhibition efficiency[9]. Thus TU, which adsorbs on the metal surface through the sulphur atom, is balanced by the two amino groups with sulphur at the centre. When phenyl group is attached at one of the nitrogen atoms of the TU, the molecule is imbalanced, projecting more surface area to cover the surface of the electrode and, therefore, may exhibit better inhibition than the thiourea itself[3]. Our results are in good agreement with this view where PhTU shows enhanced inhibition over the TU. One of the reasons of the improved inhibition efficiency of the PhTU may also be due to the fact that this compound, in addition to adsorption through functional sulphur atom, may also get adsorbed through the π electron clouds of the phenyl ring parallel to the electrode surface. The better inhibition performance of Ph-TU in 1% HCl and 1 : 3-di-*o*-tolTU in 5% HCl than other compounds may be attributed to the large molecular area projected by these two compounds on the metal surface[3].

It may also be evident from Table 1 that effectiveness of the compounds increases with the increase in the temperatures from 25° to 45°C except for urea. Increase in inhibitor efficiency at higher temperatures is rarely observed, but was observed by Hoar and Holliday[5] while studying the inhibition of the acid corrosion of mild steel by *o*-tolTU. They have suggested that this enhancement in inhibitive efficiency at higher temperatures may be due to the higher activation energy available for adsorption, and the higher rate of diffusion of bulky inhibitor molecules. We have observed that the inhibitive efficiencies continue to increase with increase in temperature with the smaller inhibitor molecules such as TU, as well as with the larger molecules such as disubstituted tolTU, although the relative increase is greater with the larger molecule. This is further confirmed by heat of adsorption (Table 1). High value of heat of adsorption is observed for higher temperature range (35°–45°C), suggesting that more molecules may be adsorbed on the metallic surface by increasing temperature. Simultaneously the greater surface area projected by the larger molecules on the metal surface is also responsible for the greater relative increase. Poor inhibition exhibited by urea at 45°C is probably due to the formation of corrosion-promoting species by decomposition of urea at higher temperature.

TABLE 3
PERCENTAGE INHIBITION EFFICIENCIES (E) OF THE INHIBITORS IN 1% AND 5% HYDROCHLORIC ACID AT 35°C

Inhibitors	1% HCl			5% HCl		
	Time in hrs			Time in hrs		
	24	48	72	24	48	72
		E			E	
Urea	7	16	15	5	12	10
Thiourea	24	47	42	26	18	12
Phenyl thiourea	30	59	54	24	40	30
o-tolTU	25	39	38	3	6	2
m-tolTU	19	35	33	2	4	2
p-tolTU	25	47	45	23	20	10
1:3-di-*o*-tolTU	24	44	36	30	31	23
1:3-di-*m*-tolTU	25	35	36	28	28	19
1:3-di-*p*-tolTU	37	46	41	–3	–2	–5

Table 3 gives the relation between the exposure period and inhibition efficiency of the molecules in 1% and 5% hydrochloric acid at 35°C. The extent of the effect of exposure period taken on inhibition is carried out by taking the concentration of the inhibitor which gives optimum percentage inhibition efficiency. It is evident from the Table that all molecules give better protection for 48 h exposure period and thereafter a decrease in protectability of molecules is to be observed. The extent of increment in the inhibition efficiency for 1% hydrochloric acid is more than the extent of decrease, whereas a reverse order has been observed in 5% hydrochloric acid. In the case of urea, PhTU, *m*-tolTU and *p*-tolTU, the inhibition efficiency for 48 h becomes approximately double that of 24 h. All the compounds are most effective after a period of 48 h. It is possible that the inhibitors form a film of optimum resistance after a certain period, say, 48 h. After this they may become gradually desorbed; or the decrease in efficiency may be due to degradation (oxidation/reduction) of the compounds in the presence of acid solution, or both factors may play a part.

Adsorption plays an important role in the inhibition of metallic corrosion by organic inhibitors. Many investigators have used Langmuir's adsorption isotherm to study inhibitor characteristics[5, 10, 11]. Assuming that the inhibitors adsorbed on the metal surface decrease the surface area available for cathodic or anodic reactions to take place. Hoar and Holliday[5] have shown that the Langmuir isotherm:

$$\log \frac{\theta}{1-\theta} = \log A + \log C - \frac{Q}{2.3RT}$$

should give a straight line of unit gradient for the plot of $\log \theta/(1-\theta)$ vs log c, where

$$\theta = 1 - \frac{\text{inhibited corrosion rate}}{\text{uninhibited corrosion rate}}$$

A = a temperature – independent constant

C = bulk concentration of the inhibitors in mol/lit.

Q = the heat of adsorption

The corresponding plots at 25°, 35° and 45°C for 1100 alloy have been shown in Figs. 1 and 2. The plots are linear and only 1:3-di-*m*-tolTU and 1:3-di-*p*-tolTU

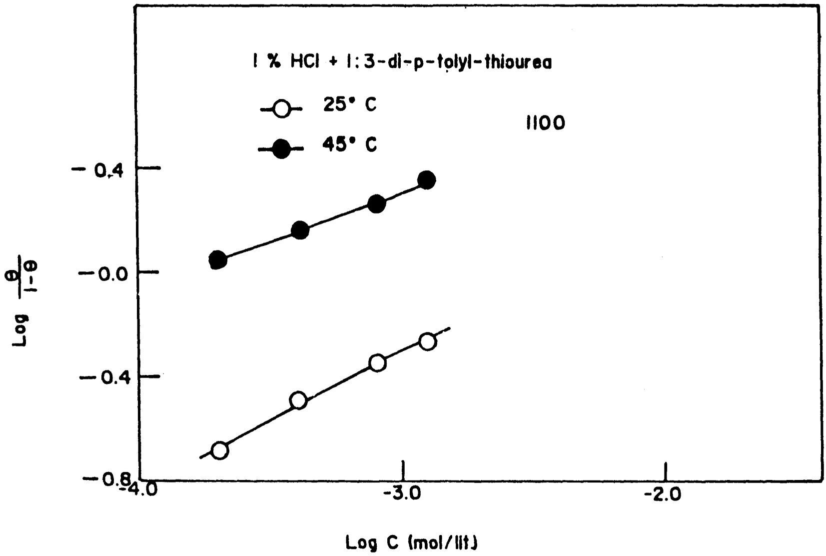

Fig. 1 Langmuir adsorption plots at 35°C

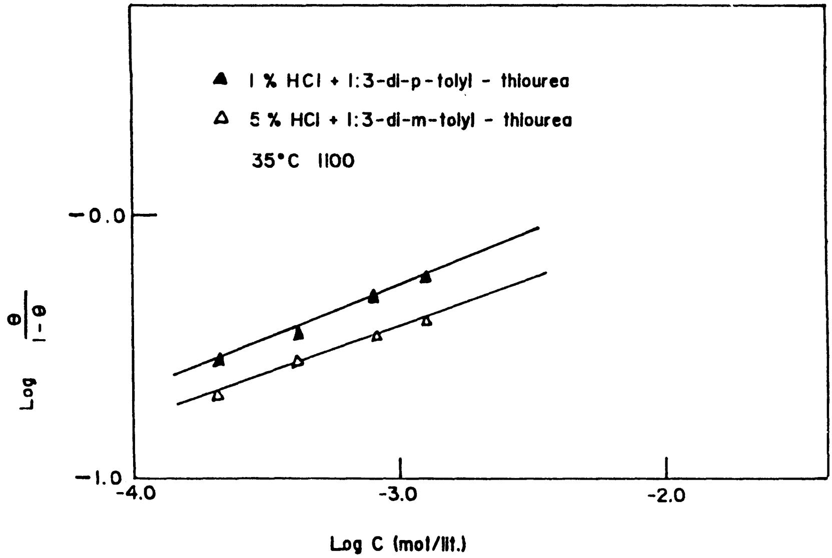

Fig. 2 Langmuir adsorption plots for 1:3-di-*p*-tolyl thiourea at 25°C and 45°C

obey the isotherm equation at all temperatures in 5% and 1% hydrochloric acid solution respectively. The plots for 1:3-di-*m*-tolTU at 25° and 45°C are not given in the figures. This shows that other compounds do not adsorb on the metallic surface. Their tendency to decrease corrosion rate may be due to the formation of ionizable salts with the acid as suggested by Mann[12].

The plot of log θ/(1 – θ) vs log C for these two compounds is linear, but the gradients are not equal to unity, as is expected for the ideal Langmuir adsorption isotherm equation. This deviation from unity may be explained on the basis of the interaction among the adsorbed species on the metal surface. It has been postulated in the derivation of the Langmuir isotherm equation that the adsorbed molecules do not interact with one another, but this is not true in the case of organic molecules having polar atoms or groups which are adsorbed on the anodic and cathodic sites of the metal surface. Such adsorbed species may interact by mutual repulsion or attraction. It is also possible for inhibitor molecules to interact, that are adsorbed on anodic and cathodic sites respectively. These interactions would affect the heat of adsorption of the inhibitors. If the interaction is repulsive in nature, the heat of adsorption would be negative, and vice versa. Interaction factor really seems to be a criterion for the non-ideal behaviour of the compound because the slopes observed are 0.50, 0.38 and 0.40 for 1:3-di-*p*-tolTU at 25°, 35° and 45°C respectively. This is because of the fact that at 25°C, there being a lesser population of the adsorbed species, the probability of their interaction being less, and thus slope increases.

It was observed that percentage inhibition efficiencies of the inhibitors decrease with the increase in the concentrations of the inhibitors at all the temperature studied in both the acid solutions. 1:3-di-*p*-tolTU and 1:3-di-*m*-tolTU do not show such behaviour in 1% and 5% hydrochloric acid respectively. Many earlier workers have reported the corrosion acceleration in the presence of higher concentrations of the TU for other systems[13, 14]. It has been suggested that the corrosion acceleration by TU at the higher concentrations is due to the formation of the corrosion promoting species HS^- and S^{2-} in non-oxidising acids. It seems here also in the case of TU and its derivatives that the formation of HS^- and S^{2-} species is responsible for the corrosion acceleration.

The cathodic and the anodic polarisation curves in the presence of that concentration of the inhibitors for which the observed efficiency is maximum at 35°C have been shown in Figs. 3 and 4 in 1% hydrochloric acid. The plots for 5% hydrochloric acid are not plotted because all the additives show the same trend of polarisation. By scrutinizing the figures, the following observations can be made:

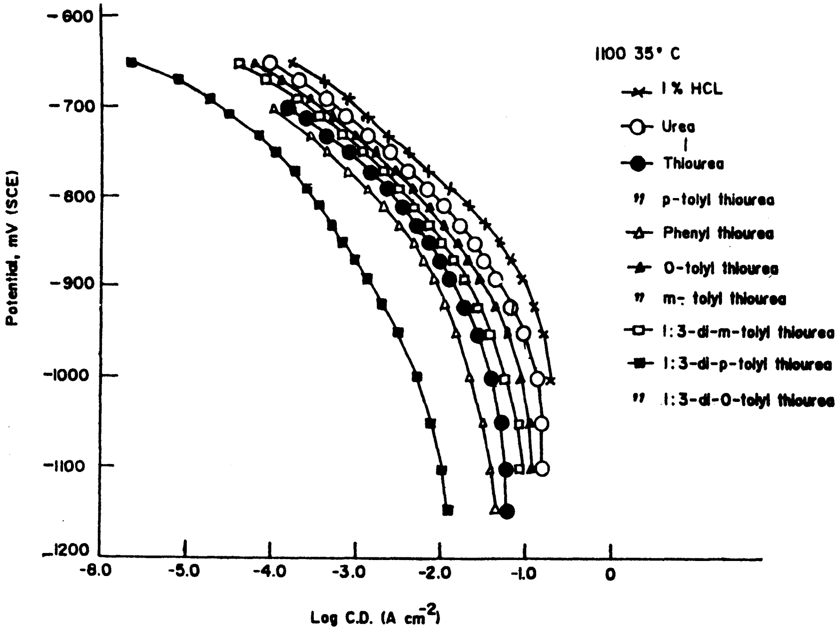

Fig. 3 Cathodic polarisation of 1100 aluminium in the presence of inhibitors at 35°C

(1) The cathodic polarisation curves in the presence of the inhibitors are almost similar to the curves in their absence;

(2) The anodic and cathodic polarisation curves in the presence of the inhibitors are shifting towards left side (*i.e.* lower current density side) to the curve in their absence. This shifting is more pronounced for the cathodic curves than that for the anodic curves.

The parallel cathodic polarisation lines show that the inhibitors do not interfere with the cathodic reaction taking place on the metal surface. It is evident from Table 4 that the inhibitors have shifted the steady state corrosion potential in the active direction. These results indicate that the inhibitors simply block the cathodic sites on the metal surface. This simple blocking effect decreases the number of

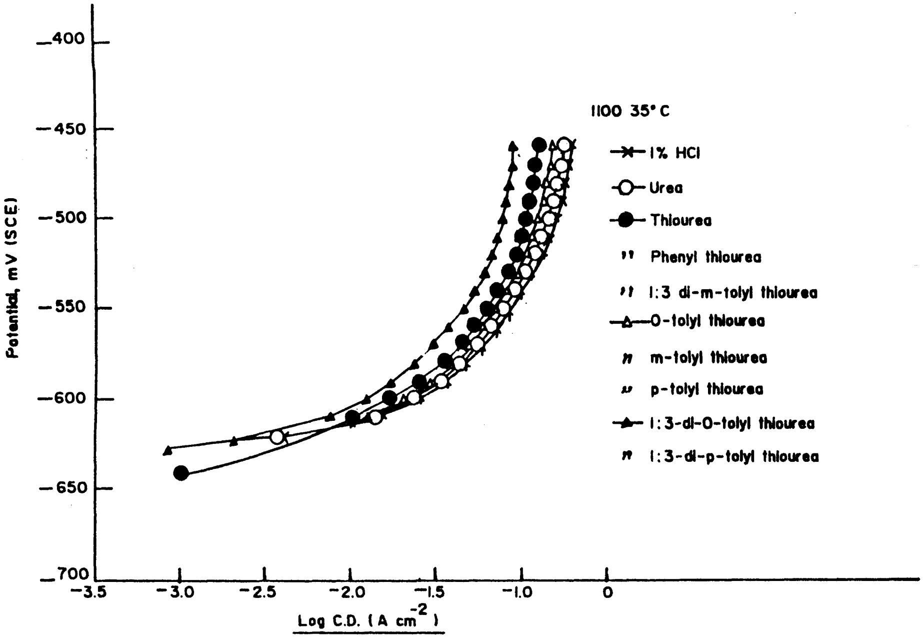

Fig. 4 Anodic polarisation of 1100 aluminium in the presence of inhibitors at 35°C

the surface metal atoms at which corrosion reactions can take plate smoothly in the absence of inhibitors, and hence decrease in the corrosion rate is observed.

TABLE 4
STEADY STATE CORROSION POTENTIAL IN THE PRESENCE OF OPTIMUM CONCENTRATIONS OF THE INHIBITORS AT 35°C

Inhibitors	Steady state	Corrosion potential (–V)
	1% HCl	5% HCl
Uninhibited	0.639	0.670
Urea	0.670	0.675
Thiourea	0.674	0.684
Phenyl thiourea	0.675	0.688
o-tolTU	0.650	0.674
m-tolTU	0.657	0.681
p-tolTU	0.671	0.677
1:3-di-*o*-tolTU	0.675	0.684
1:3-di-*m*-tolTU	0.663	0.682
1:3-di-*p*-tolTU	0.650	0.680

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