Mechanism of Corrosion Inhibition of Stainless Steel

R.M. OZA, P.C.VADHER, A.B.PATEL and J.C.VORA

Chemistry Department, University School of sciences, Gujarat University,Ahmedabad-9 (India)

The action of thiourea and its derivatives is studied for corrosion inhibition of A.I.S.I. type 304 stainless steel in hydrochloric acid solutions. The mechanism of inhibition has been discussed.

Thiourea and its derivatives have been extensively studied as corrosion inhibitors of many metals in acedic solutions. The mechanism of inhibition of these compounds is not clearly revealed. In present investigation an attempt has been made to evaluate the inhibitive power and mechanism of inhibition of stainless steel (304) in hydrochloric acid solutions by thiourea derivatives.

EXPERIMENTAL

A.I.S.I. type 304 stainless steel (supplied by M/s. Hindustan Steel Ltd., Durgapur, India) used for this study had following chemical composition:

Cr	Ni	Mn	C	P	S	Si
18.54,	9.54,	1.4,	0.06,	0.024,	0.013,	0.41 %

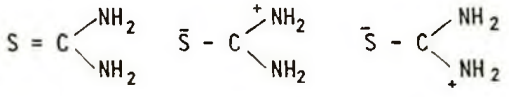
The sheets were rolled and annealed at 108° C. Specimens (2.54 x 2.54 cm, 18 S.W.G.) were totally immersed in beakers containing 250ml of different corroding media (2.5 M, 5.0 M and 7.5 M hydrochloric acid, with and without inhibitors). Experiments were carried in triplicate and the mean value has been reported. The reproducibility of percentage of inhibition is ± 2. Preparation, testing and specimens cleaning preocedure were adopted as described!

RESULTS AND DISCUSSION

Corrosion inhibition by organic compounds is generally attributed to interaction by absorption between inhibitor and metal surface[2]. The adsorption may range from single adsorption to a formation of true physical barriers.

The adsorption is essentially chemisorption. Generally lewis acid-base type bond[3] is formed, with the inhibitor (electron donor) and metal (electron aceptor), the strength of the bond depending upon the characterstics of both the adsorbent and adsorbate.

Several workers have studied the mechanism of action of thiourea and its derivatives on metals[4-12]. The data regarding mode of adsorption from direct studies are yet to come; the indirect evidence are from the studies of spectra of co-ordination compounds. The structure of thiourea is hybrid of the structures I, II and III, each contributing roughly an equal amount.



I II III

The infra-red spectra of thiourea complexes show that most of the metals form M-S bonds, nitrogen atom remaining mostly inert[13-17]. A few metals appear to form M - N bond[18].

It is interesting to examine the results obtained in the present investigation in the light of the above information. In 2.5, 5.0 and 7.5 M hydrochloric acid, thiourea accelerates corrosion at its lower concentrations. The acceleration at lower concentration has been attributed mainly to H_2S produced by cathodic reaction of thiourea[19].

$$H_2N - CS - NH_2 + 6H^+ + 2HCl \dashrightarrow NH_4Cl + CH_3NH_3Cl + H_2S$$

H_2S acts as an anodic depolarizer. The inhibitive power of thiourea and its derivatives, in general, increases with increase in concentration of acid, as well as that of the inhibitors.

Sulphur atom of thiourea contains two lone pairs of electrons, one of which can be made availabe for the bond formation with the metal atom. Such chemisorption is responsible for its inhibitive action. Substituted thioureas, inhibit corrosion even at their lower concentrations.

Substitution of a group or radicals in the molecule can bring out a change of the elctron density over the nitrogen atom[5] but only very little at the sulphur atom. If adsorption takes place only through the sulphur atom, there should not be too high a change in overall inhibition with the substituted thioureas. But it is observed that the inhibitive power of methyl

TABLE 1

EFFECT OF INHIBITOR ON CORROSION OF A.I.S.I. TYPE 304 STAINLESS STEEL

Duration: 12 hrs Temp: 38° + 1°C

inhibitor concentration per litre	2.4 M HCl Loss mg/dm^2/hour A	2.4 M HCl Inhibition (%) B	5.0 M HCl Loss mg/dm^2/hour A	5.0 M HCl Inhibition (%) B	7.5 M HCl Loss mg/dm^2/hour A	7.5 M HCl Inhibition (%) B
A= Loss mg/dm^2/hour B = Inhibition %						
Thiourea						
00	23.2	-	160	-	1500	-
0.13	48.4	AC	409	AC	1915	AC
1.3	27.8	AC	220	AC	1720	AC
13.0	23.9	AC	54	68	660	59
130.0	20.0	14	46	73	370	77
Methyl Thiourea						
0.11	18.1	22	74	56	360	78
1.1	12.3	47	100	39	460	70
11.0	5.8	75	28	83	170	89
110.0	1.0	78	12	93	60	96
Ethyl Thiourea						
0.096	54	AC	176	AC	1800	AC
0.96	41	AC	195	AC	1376	15
9.6	9.7	58	58	65	960	41
96.0	7.7	67	19	89	227	86
Diethyl Thiorea						
0.076	29.7	AC	52	69	270	83
0.76	12.3	47	23	86	110	93
7.6	8.4	64	10	94	20	99
76.0	5.8	75	9	95	12	99
Dibutyl Thiourea						
0.059	22.6	3	59	65	320	80
0.59	8.4	64	6	96	40	98
5.9	4.5	81	5	97	22	99
59.0	3.9	83	4	98	20	99
Allyl Thiourea						
0.086	23.9	AC	67	60	250	84
0.86	16.1	31	30	82	120	93
8.6	8.4	64	18	89	50	97
86.0	6.5	72	10	94	20	99
Phenyl Thiourea						
0.064	16	30	134	20	1190	26
0.64	5.8	75	19	89	490	69
6.4	3.8	84	5	97	30	98
64.0	2.6	89	3	98	10	99
Diphenyl Thiourea						
0.037	16	30	132	21	630	61
0.37	14.8	36	118	30	270	83
3.7	6.5	72	52	69	40	98
37.0	3.2	86	12	93	30	98
N-N'-DI-O-Tolyl Thiourea						
0.039	31.6	AC	141	16	280	83
0.39	14.8	36	33	80	180	89
3.9	7	69	15	91	40	98
39.0	7	69	9	95	20	99
N-N'-Di-P-Tolyl Thiourea						
0.039	80	AC	180	AC	600	63
0.39	70	AC	190	AC	620	60
3.9	100	AC	210	AC	600	63
39.0	140	AC	270	AC	590	63

TABLE 2

Inhibitor	Inhibition %	H_2S gas evolved or not
Thiourea	82	Yes
Methyl Thiourea	82	Nil
Ethyl Thiourea	80	Nil
Diethyl Thiourea	85	Nil
Dibutyl Thiourea	94	Nil
Allyl Thiourea	95	Nil
Phenyl Thiourea	84	Nil
Diphenyl Thiourea	68	Nil
N-N'-Di-p-Tolyl Thiourea	67	Yes
N-N'-Di-o-Tolyl Thiourea	80	Yes

thiourea is higher than that due to thiourea. Presence of methyl group increases the electron density over the nitrogen atom without any such change at the sulphur atom. This suggests that nitrogen atom may be playing some role in chemisorption. The effect of ethyl group on the nitrogen is similar to that of methyl group but to a lesser extent. It is observed that inhibition by ethyl thiourea is lower than that of methyl thiourea. Diethyl thiourea affects the

electron density over both the nitrogen atoms and inhibition action is higher than that of ethyl thiourea. In phenyl thiourea, the electron density at nitrogen atoms is lower as phenyl group is an electron withdrawing group. However, it has high coverage area compared to the methyl group and this is responsible for the higher inhibitive power of phenyl thiourea. Diethyl thiourea has better inhibitive power than ethyl thiourea and diphenyl thiourea is better inhibitor than phenyl thiourea. This can be explained on the above lines. Diphenyl thiourea has inhibitive power lower than diethyl thiourea. This may be because the electron density at both the nitrogen atoms has been decreased in diphenyl thiourea.

N-N' di-O-tolyl thiourea is somewhat better inhibitor than diphenyl thiourea. This appears principally because of the presence of electron repelling methyl group in the benzene ring. This results in some increase in electron density over the nitrogen atom.

Some discrepancy appears in the behaviour of N-N' di-p-tolyl thiourea which shows acceleration of corrosion at lower concentrations, a behaviour similar to that of thiourea. It would be interesting to consider the following experimental results in this connection. Stainless steel specimens were completely immersed in wide mouth stoppered bottles containing 5.0 M HCl solutions (250 ml). Inhibitors (Mol/1 x 10^{-4}) were added to these solutions. The observations were made regarding the inhibition (%) and evolution of H_2S gas (qualitatively). Hydrogen gas was passed through these solutions and the gases evolved were then passed through antimony trichloride solution (just made sufficiently acidic with HCl to keep $SbCl_3$ in solution). The observations made are reported in tables 1 and 2.

The order of decreasing inhibition is as follows:

Allyl thiourea $\geqslant$ Dibutyl thiourea $>$ Phenyl thiourea $\geqslant$ Diethyl thiourea $>$ Methyl thiourea = Thiourea $>$ Ethyl thiourea $\geqslant$ N-N' -Di-o-tolyl thiourea $>$ Diphenyl thiourea $\geqslant$ N-N' -Di-p-tolyl thiourea.

The results show that, in general, aliphatic substitution at nitrogen atom give better inhibition than the aromatic substituion. It is interesting to note that the liberation of H_2S gas has no adverse effect on inhibition. Thiourea and N-N' -Di-p-tolyl thiourea, which show acceleration of corrosion in open beaker systems, inhibit corrosion in absence of oxygen. Even though H_2S is evolved in these cases, there is no adverse effect on inhibition. In closed systems where availability of atmospheric oxygen is considerably reduced, acceleration of corrosion stops and the inhibition becomes prominent. It will be apt to assume that acceleration of corrosion observed by earlier works may be ascribed to cathodic depolarization due to atmospheric oxygen rather than anodic depolarization due to liberated H_2S. This is in agreement with the conclusion drawn by Antropov[20] who observed high coefficient of inhibition in HCl solutions saturated with H_2S.

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