Alicyclic Compounds as Corrosion Inhibitors for Aluminium 57S in Hydrochloric Acid Solutions

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Cyclohexanone, cyclohexanol, methylcyclohexanol and cyclohexylamine are investigated as inhibitors of corrosion of aluminium 57S in hydrochloric acid solutions. Cyclohexanone is a satisfactory inhibitor whereas the performance of cyclohexanol is less satisfactory than that of cyclohexanone. In 1.0 N hydrochloric acid, the efficiency of inhibitors improves with temperature in the range 35° - 55°C. All the four substances are predominantly cathodic inhibitors and reduce the current needed for cathodic protection of Aluminium 57S in 2.0 N hydrochloric acid. The difference effect is negative in inhibited 2.0 N hydrochloric acid but positive in uninhibited 2.0 N hydrochloric acid.

This paper reports retardation of corrosion of aluminium 57S in hydrochloric acid by cyclohexanone, cyclohexanol, methylcyclohexanol and cyclohexylamine.

EXPERIMENTAL

Aluminium alloy Indal-57S manufactured by M/s. Indian Aluminium Co. is used widely. The specifications given by the company are:

Indal 57S - half hard.

Mg-2.0%, Mn-0.3%, traces of Si, Cu and Ti, Aluminium remainder.

This material was selected for study. The preparation of specimens and corrosion studies were carried out as already described(1).

RESULTS AND DISCUSSION

The corrosion of aluminium 57S in hydrochloric acid increases with time as well as with acid concentration. The effect of time on inhibitor efficiency is given in Table 1. Influence of

TABLE 1

EFFECT OF TIME AND HCL CONCENTRATION ON THE CORROSION OF ALUMINIUM 57S

Temperature: 35° ± 0.1°C

		Weight loss in mg/dm² and (% corrosion efficiency) for different times								
Time in minutes		1	2	5	10	15	30	60	120	180
1.0 N HYDROCHLORIC ACID		-	-	-	14.9	-	61.0	146.6	315.2	461.5
Cyclohexanol	43.8 ml/l	-	-	-	11.9	-	26.0	37.1	46.1	63.4
		-	-	-	(20.0)	-	(57.3)	(74.7)	(85.4)	(86.3)
Cyclohexanone	26.1 ml/l	-	-	-	5.7	-	11.7	16.8	31.2	39.6
		-	-	-	(61.8)	-	(80.9)	(88.5)	(90.1)	(91.4)
Methylcyclohexanol	8.7 ml/l	-	-	-	10.6	-	20.9	34.1	56.0	61.5
		-	-	-	(29.1)	-	(65.8)	(76.7)	(82.2)	(86.7)
Cyclohexylamine	26.1 ml/l	-	-	-	5.2	-	14.1	19.3	58.3	74.5
		-	-	-	(65.0)	-	(76.9)	(80.0)	(81.5)	(83.9)
2.0 N HYDROCHLORIC ACID		-	-	15.2	138.2	371.0	983.7	3139.0	-	-
Cyclohexanol	34.8 ml/l	-	-	11.4	37.2	68.3	225.7	286.2	-	-
		-	-	(25.0)	(73.1)	(81.5)	(77.1)	(90.9)	-	-
Cyclohexanone	34.8 ml/l	-	-	11.1	16.8	31.4	140.9	233.9	-	-
		-	-	(26.8)	(87.8)	(91.5)	(85.7)	(92.6)	-	-

Table 1 contd.

		Weight loss in mg/dm² and (% corrosion efficiency) for different times								
	Time in minutes	1	2	5	10	15	30	60	120	180
Methylcyclohexanol	8.7 ml/l	-	-	13.5	58.8	121.9	238.5	339.6	-	-
		-	-	(10.7)	(57.4)	(67.1)	(75.8)	(89.2)	-	-
Cyclohexylamine	26.1 ml/l	-	-	10.0	22.5	58.0	155.0	308.0	-	-
		-	-	(33.9)	(83.9)	(84.3)	(84.2)	(90.3)	-	-
3.0 N HYDROCHLORIC ACID		-	-	459.9	2476.0	5226.0	-	-	-	-
Cyclohexanol	34.8 ml/l	-	-	23.3	172.4	439.8	1548.0	-	-	-
		-	-	(94.9)	(93.2)	(91.6)	-	-	-	-
Cyclohexanone	43.5 ml/l	-	-	6.5	34.9	137.9	760.7	-	-	-
		-	-	(98.6)	(98.6)	(97.4)	-	-	-	-
Methylcyclohexanol	17.4 ml/l	-	-	135.5	338.7	1194.0	2883.0	-	-	-
		-	-	(11.2)	(86.3)	(77.2)	-	-	-	-
Cyclohexylamine	34.8 ml/l	-	-	24.4	156.1	468.6	1502.0	-	-	-
		-	-	(94.7)	(93.7)	(91.1)	-	-	-	-
4.0 N HYDROCHLORIC ACID		29.0	306.2	5625.0	-	-	-	-	-	-
Cyclohexanol	34.8 ml/l	2.7	12.2	104.3	987.8	-	-	-	-	-
		(90.7)	(96.0)	(98.1)	-	-	-	-	-	-
Cyclohexanone	43.5 ml/l	2.7	4.9	21.1	143.1	-	-	-	-	-
		(90.7)	(98.4)	(99.6)	-	-	-	-	-	-
Methylcyclohexanol	17.4 ml/l	7.6	37.9	874.0	2740.0	-	-	-	-	-
		(73.8)	(87.6)	(84.0)	-	-	-	-	-	-
Cyclohexylamine	34.8 ml/l	2.7	13.0	183.2	1220.0	-	-	-	-	-
		(90.7)	(95.7)	(96.7)	-	-	-	-	-	-

TABLE 2

TAFEL PARAMETERS AND EFFICIENCY OF INHIBITORS IN 1.0 N HYDROCHLORIC ACID

Inhibitor and inhibitor concentration	Tafel slope 'b'		Energy transfer coefficient (cathodic)	Corrosion Current mA cm^{-2} from		Inhibitor efficiency from % i_{corr}		Inhibitor efficiency from loss in weight method
	Anodic (V)	Cathodic (V)		Extrapolation of cathodic Tafel line	Intersection of cathodic and anodic Tafel lines at open circuit potential	from column 5	from column 6	
Nil	0.12	0.15	0.41	3.57	5.32	-	-	-
Cyclohexanol 34.8 ml/l	0.1	0.16	0.38	1.62	2.76	54.6	57.8	20 - 85
cyclohexanone 26.1 ml/l	0.08	0.22	0.28	0.731	0.974	79.5	81.7	61 - 90
Methylcyclohexanol 8.7 ml/l	0.08	0.18	0.34	1.30	1.94	63.6	63.4	29 - 82
Cyclohexylamine 26.1 m/l	0.06	0.17	0.36	0.812	1.30	77.3	75.6	65 - 81

Current density on cathode and anode potentials of aluminium 57S in 1.0N hydrochloric acid in absence and presence of inhibitors is also studied (Fig.1). The Tafel parameters and efficiencies of inhibitors calculated from polarization data are given in Table 2. Polarization measurements indicate that the corrosion process is predominantly cathodically controlled.

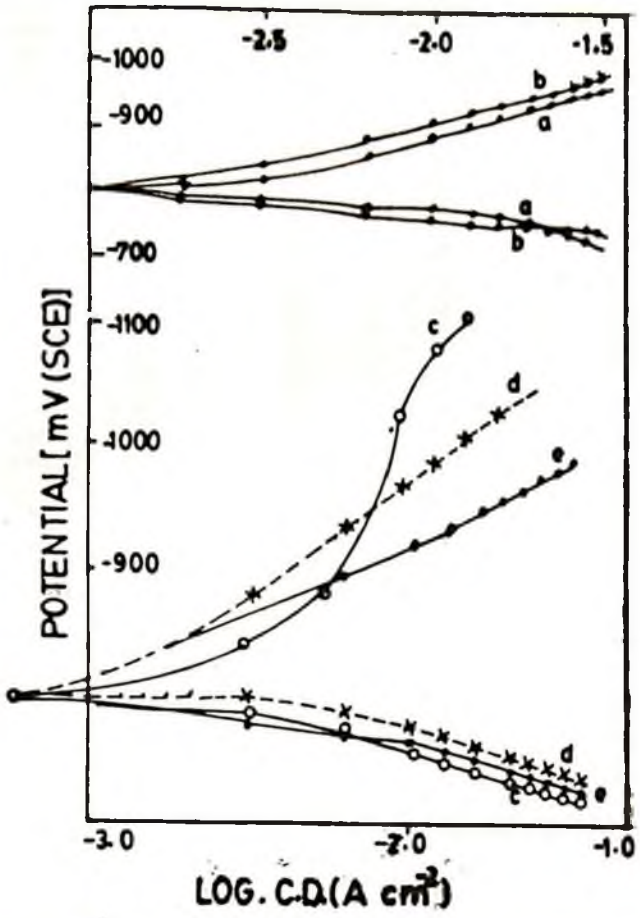


Fig.1 Influence of current density on cathode and anode potentials of Al-57 S in 1.0 N Hydrochloric acid solution in the presence and absence of Inhibitors:
(a) Uninhibited 1.0 N HCl (Blank)
(b) Cyclohexanol 34.8 ml/l
(c) Cyclohexanone 26.1 ml/l
(d) Methylcyclohexanol 8.7 ml/l
(e) Cyclohexylamine 26.1 ml/l

Cyclohexanone is a satisfactory inhibitor for the corrosion of aluminium 57S in hydrochloric acid solutions. Both for five and ten minutes durations, the efficiency of cyclohexanone improves with increase in acid concentration. The addition of 26.1 ml/l cyclohexanone to 1.0N hydrochloric acid increases cathode polarization considerably as compared to anode polarization. In general in 1.0, and 2.0 N solutions of hydrochloric acid, its efficiency increases with the passage of time, whereas in 3.0 and 4.0 N it is high at all measured times.

The behaviour of cyclohexanol is analogous to that of cyclohexanone but in general, its performance is less satisfactory than that of cyclohexanone.

Even at as low a concentration as 4.35 ml/l methylcyclohexanol affords a very good protection to aluminium 57S in 1.0 and 2.0 N hydrochloric acid. The effect of methylcyclohexanol is not immediate in 1.0, 2.0 and 3.0 N solutions of hydrochloric acid but its efficiency improves with the passage of time. In 4.0 N hydrochloric acid, its efficiency ranges from 74-88% for the periods of study. Even at as low a concentration as 8.70 ml/l^{-1}, methylcyclohexanol induces considerable increase in cathode polarization whereas there is very little effect of the inhibitor on the anode polarization.

The efficiency of cyclohexylamine improves with the passage of time, increase in inhibitor concentration and acid concentration. At lower current densities, cyclohexylamine increases the polarization of both the cathode and the anode but its effect at higher current densities is not of that magnitude.

The values of Tafel parameters and the efficiencies of the inhibitor in 1.0 N hydrochloric acid, evaluated from :(1) extrapolation of cathode Tafel line to the open circuit potential and (2) from the intersection of cathodic and anodic Tafel lines at the open circuit potential are shown in Table 2.

The effect of temperature on the performance of inhibitors in 1.0 N hydrochloric acid was investigated in the temperature range 35°-55°C.

The efficiency of cyclohexanol increases from 40°-55°C whereas the efficiency of cyclohexanone and methylcyclohexanol increases with increase in entire temperature range (35°-55°C). The efficiency of cyclohexylamine ranges from 77-68, 82-67, 81-75 and 84-77% respectively for 30, 60, 120 and 180 minutes durations.

The activation energies of the inhibitors were evaluated from plots of 1/T against log corrosion rates according to the Arrhenius equation. Results are given in Table 3. For all the inhibitors, the values of activation energy are lower in the presence of inhibitors than those in its absence, indicating that the inhibitors become more effective as the temperature rises.

The activation energies of inhibited reactions at high coverages can be either larger or smaller than the uninhibited reaction. Machu (2) had reported that for powerful inhibitors, the activation energy is lower for inhibited than for uninhibited reaction. This type of behaviour has been explained by Putilova (3) as due to an increase in surface area of metal covered by inhibitror molecules as the temperature rises.

TABLE 3

ACTIVATION ENERGIES IN THE PRESENCE AND ABSENCE OF INHIBITORS (In kCal mole/1)

	Minutes			
	30	60	120	180
Nil	13.8	12.0	11.96	11.96
Cyclohexanol 34.8 ml/l	6.44	5.52	5.98	6.91
Cyclohexanone 26.1 ml/l	10.59	8.75	10.14	8.75
Methylcyclohexanol 8.7 ml/l	7.83	4.6	8.75	8.75
Cyclohexylamine 26.1 ml/l	13.74	10.14	11.0	11.0

However, Riggs (4) suggested that at high coverages, the extent of adsorption is no longer rate determining.

Studies of cathodic protection to aluminium 57S in 2. 0 N hydrochloric acid indicate that addition of inhibitors considerably lowers the protective current (Table 4).

Results obtained under external anodic current, show that the difference effect is negative for aluminium 57S in 2.0 N hydrochloric acid whereas in the presence of the inhibitors, the difference effect becomes positive. The values of difference effect coefficient were evaluated according to the equation -

$$K_{DE} = \frac{\Delta i \text{ (Corr)}}{\Delta i \text{ (Pol)}}$$

The values of K_{DE} in uninhibited 2.0 N hydrochloric acid and in the presence of cyclohexanone, cyclohexanol, methylcyclohexanol and cyclohexylamine are - 0.10, + 0.67, + 0.70 + 0.67 and + 0.65 respectively.

TABLE 4

EFFECT OF CURRENT DENSITY OF CATHODE WEIGHT LOSS (CATHODIC PROTECTION)

Aluminium-57S Acid concentration : 2.0 N
Time : 30 minutes

Inhibitor concentration	Current density A dm/2	Weight loss m dm/2	Protection % due to Current	Protection % due to Current Inhibitor
Nil	0.0	1071	-	-
	0.081	985	8	-
	0.162	682	36	-
	0.325	553	48	-
	0.487	360	66	-
	0.650	181	83	-
	0.812	0	100	-
Cyclohexanol 34.8 ml/l	0.0	248	-	77
	0.325	143	42	87
	0.406	124	50	88
	0.487	20	92	98
	0.650	0	100	100
Cyclohexanone 34.8 ml/l	0.0	157	-	85
	0.244	21	87	98
	0.325	7	96	99
	0.357	0	100	100
Methylcyclohexanol 8.7 ml/l	0.0	228	-	79
	0.325	147	36	86
	0.406	85	63	92
	0.487	0	100	100
Cyclohexylamine 26.1 ml/l	0.0	166	-	85
	0.163	90	46	92
	0.325	44	74	96
	0.406	0	100	100

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