N-SUBSTITUTED ANILINES AS CORROSION INHIBITORS FOR ALUMINIUM-2S IN HYDROCHLORIC ACID

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Abstract:

Substitution of aminohydrogen atom in aniline is beneficial to inhibitor action. The lengthening of side chain improves inhibitor efficiency as indicated by loss in weight data, polarisation measurements and cathodic protection studies.

Introduction:

Mann[1], Antonucii[2], Nathan[3], Ride[4], Hackerman[5], Antropov[6] investigated N-substituted methyl and ethylanilines as corrosion inhibitors for iron in acidic media. The present study was undertaken to investigate the retardation of corrosion of Aluminium-2S in hydrochloric acid.

Aluminium alloy Indal-2S manufactured by Messrs. Indian Aluminium Company was selected for the study in view of its widespread use. It has been specified as follows by the manufacturing company:

Indal 2S — half hard, aluminium 99% Fe—0.4%, Si—0.3%, Mn and Mg—0.1% Cu, Ca, Ti—traces

The preparation of specimens and corrosion studies were carried out as described in our previous publication[7].

Observations:

The effect of time on efficiency of inhibitors in 1-4N solutions of hydrochloric acid is given in Table 1. It can be seen that aniline is not a satisfactory inhibitor. Substitution of a hydrogen atom of primary amino group in aniline improves its inhibitor action, e.g., in 1.0N HCl for 120 minutes duration of 43.5 ml/l concentration the efficiencies, of aniline and methylaniline are 34% and 60.0%. In general, the efficiency of methyl aniline, decreases with time in 1.0 N HCl where as in 3.0 N HCl a reverse behaviour is observed. In 2.0 N and 4.0 N HCl solutions the efficiency ranges from 78-87% and 62-79% respectively.

TABLE I

	1 min.	2 min.	5 min.	10 min.	15 min.	30 min.	60 min.	120 min.	180 min.
1.0N HCl: Nil	—	—	—	33.2 (—)	—	113.4 (—)	127.5 (—)	151.2 (—)	172.8 (—)
Methyl-aniline ... (43.5 ml/l) ...				10.2 (69.1)	—	41.6 (63.3)	57.5 (54.7)	61.8 (60.0)	87.5 (49.9)
Dimethyl-aniline ... (43.5 ml/l) ...	—	—	—	15.1 (54.4)	—	60.8 (46.4)	67.5 (39.2)	110.7 (26.8)	133.9 (22.5)
Ethyl-aniline ... (43.5 ml/l) ...	—	—	—	5.7 (82.9)	—	27.5 (75.7)	34.5 (72.9)	40.8 (73.0)	54.5 (68.5)
Diethyl-aniline ... (43.5 ml/l) ...	—	—	—	7.9 (76.4)	—	41.3 (63.6)	50.5 (66.4)	51.8 (65.7)	66.6 (61.4)

TABLE I (Contd.)

2.0N HCl:									
Nil ...	—	—	58.9 (—)	568.5 (—)	888.4 (—)	3105 (—)	...	...	—
Methyl-aniline ... (43.5 ml/l) ...	—	—	12.7 (78.4)	70.5 (87.6)	175.0 (80.3)	640.0 (79.4)	857.0 (—)	—	—
Dimethyl-aniline ... (43.5 ml/l) ...	—	—	13.8 (76.6)	136.1 (76.1)	292.7 (67.0)	688.5 (77.8)	1366 (—)	—	—
Ethyl-aniline ... (43.5 ml/l) ...	—	—	7.3 (87.6)	66.4 (88.3)	190.7 (78.6)	461.7 (85.1)	945.5 (—)	—	—
Diethyl-aniline ... (43.5 ml/l) ...	—	—	5.7 (90.4)	66.4 (88.3)	118.5 (86.5)	284.6 (90.8)	559.9 (—)	— —	— —
3.0N HCl:									
Nil ...	—	—	343.0 (—)	4384 (—)	—	—	—	—	—
Methyl-aniline ... (43.5 ml/l) ...	—	—	157.9 (53.9)	631.2 (85.6)	1454 (—)	4143	—	—	—
Dimethyl-aniline ... (43.5 ml/l) ...	—	—	162.8 (52.5)	821.1 (81.2)	1957 (—)	5618 (—)	—	—	—
Ehtyl-aniline ... (43.5 ml/l) ...	—	—	88.3 (74.2)	559.5 87(.2)	1232 (—)	3594 (—)	—	—	—
Diethyl-aniline ... (43.5 ml/l) ...	—	—	72.9 (78.8)	520.6 (88.1)	8645 (—)	3078 (—)	—	—	—
4.0N HCl:									
Nil ...	71.0 (—)	297.0 (—)	4915 (—)	—	—	—	—	—	—
Methyl-aniline ... (43.5 ml/l) ...	14.8 (79.1)	112.3 (62.3)	1125 (77.1)	4213 (—)	—	—	—	—	—
Dimethyl-aniline ... (43.5 ml/l) ...	10.0 (85.9)	101.0 (65.9)	1360 (72.3)	4174 (—)	—	—	—	—	—
Ethyl-aniline ... (43.5 ml/l) ...	17.3 (75.9)	87.5 (70.5)	692.0 (85.9)	4092 (—)	—	—	—	—	—
Diethyl-aniline ... (43.5 ml/l) ...	4.3 (93.9)	81.5 (73.0)	852.6 (82.6)	3542 (—)	—	—	—	—	—

Dimethylaniline is not a ratisfactory inhibitor for the corrosion of Aluminium-2S in 1.0 N HCl, the efficiency being only 26.8% at 43.5 ml/l concentration of the inhibitor. At 4.35 ml/l concentration of the inhibitor, there is a slight acceleration of corrosion of Al-2S in 1.0 N HCl. However, in 2.0 N HCl the performance of dimethylaniline is better, the efficiency being 67-78% at 43.5 ml/l concentration. With the passage of time, the inhibitor efficiency decreases in 1.0 N and increases in 3.0 N HCl. In 4.0 N HCl, the efficiency ranges between 68-86% during the periods of study.

In the aromatic amines, lengthening of alkyl side chain of the secondary amine improves its inhibitor action as can be observed by comparing the results obtained with methylaniline and ethylaniline. In 1.0 N and 2.0 N HCl, from 17.4 to 43.5 ml/l concentration range, ethylaniline protects Al-2S to a greater extent than methyalaniline. In 1.0 N HCl, the efficiency of ethylaniline falls with time where as in 3.0 N HCl it increases with time. In 2.0 N and 4.0 N solutions of HCl, the efficiency ranges from 77-88% and 70-86% respectively for the periods of study.

In 1.0 N HCl, just like methylanilines, in the case of ethylanilines also the tertiary amine is less efficient than the secondary amine. However in 2.0 N HCl diethylaniline is a better inhibitor than ethylaniline which is comparable to the behaviour of alifatic ethyl amines. In 1.0 N, 2.0 N and 4.0 N solutions of hydrochloric acid, the efficiency ranges from 60-76 86-90, 73-90% respectively for the periods of the study. A noteworthy point observed by the study of ethyl and diethylaniline, is that the lengthening of side chain is favourable to inhibitor action.

The influence of current density on the cathode and anode potentials of Aluminium-2S in uninhibited 1.0 N hydrochloric acid and in the presence of methylaniline, dimethylaniline, ethylaniline, and diethyl aniline is shown in Figs. 1, 2, 3, 4 and 5 respectively. From Fig. 2, it can be seen that methylaniline exerts a predominant influence on the local cathodes. In the presence of 4.35 ml/l dimethylaniline, both the anode and the cathode are depolarised explaining the acceleration of corrosion in the presence of this concentration of inhibitor (Fig. 3). Addition of 43.5 ml/l dimethylaniline, brings about an increased cathode polarisation, whereas in general there is a slight decrease in anode polarisation (Fig. 3). Addition of 43.5 ml/l ethylaniline increases cathode polarisation up to the current density 1.948×10^{-2} amp/cm2 whereas, there is a slight decrease in anode polarisation. Subsequently, anode potential values are the same in the presence and absence of inhibitor (Fig. 4). The additional protection afforded by lengthening of alkyl side chain is explained by comparing the results of cathode polarization in the presence of 43.5 ml/l methylaniline and ethylaniline. At the current density 2.434×10^{-2} amp/cm^2, the shift in cathode potential of Al-2S in the presence of methylaniline is 60 mv, the corresponding figure for ethylaniline being 100 mv. At the current density 3.248×10^{-2} amp/cm^2, the shifts in cathode potential in the presence of ethylaniline and methylaniline are respectively 85 mv and 185 mv.

Addition of diethylaniline induces a considerable increase in cathode polarisation (Fig. 5). Just like primary aromatic amines, in the case of secondary aromatic amines also the better inhibitor action of molecules containing longer side chain is reflected by increased cathode polarisation at higher current densities.

The values of Tafel parameters, and the efficiencies of the inhibitor in 1.0 N HCl, evaluated from (1) extrapolation of cathodic 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 II. It has been found that with all the inhibitors, a good correlation is observed between efficiency of inhibitors calculated from extrapolation of cathodic Tafel line to open circuit potential with those evaluated from loss in weight method. This also indicates that the inhibitors are predominantly cathodic in action.

Plots of log surface coverage against log inhibitor concentration show that Freundlich absorption law is obeyed in 1.0 and 2.0 N HCl in the inhibitor concentration range 8.7-43.5 ml/l.

The influence of temperature on the inhibition of corrosion of Al-2S in 1.0 N hydrochloric acid is shown in Fig. 6. For 30-120 minutes, methylaniline shows higher efficiency at 35°C which decreases at 40°C, with subsequent increase in temperature the efficiency of methylaniline improves. For 180 minutes duration the efficiency of methylaniline improves with increasing temperature. While the behaviour of ethylaniline and methylaniline are analogous, ethylaniline shows a superior performance to methylaniline at all the temperatures studied. The efficiency of dimethylaniline and diethylaniline increases with increase in temperature. At all the durations studied, the performance of diethylaniline is superior to that of dimethyl-

TABLE II

TAFEL PARAMETERS AND EFFICIENCY OF INHIBITORS

Inhibitor Concentration	*Cathodic Tafel Slope b (volts*	*Energy transfer coefficient* α	*CORROSION CURRENT*		*INHIBITOR EFFICIENCY*		
			from Extrapolation of Cathodic Tafel Line	*from Intersection of Cathodic and Anodic Tafel Lines at Open Circuit Potential*	*from* (4)	*from* (5)	*from Weight Loss Data*
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Nil ...	0.15	0.41	6.49×10^{-3}	6.50×10^{-3}			
Methylaniline 43.5 ml/l) ...	0.25	0.24	3.24×10^{-3}	4.67×10^{-3}	50.1	28.1	60—69
Dimethylaniline (43.5 ml/l) ...	0.30	0.20	4.87×10^{-3}	5.19×10^{-3}	25.0	20.1	27—54
Ethylaniline (43.5 ml/l) ...	0.20	0.30	2.01×10^{-3}	3.57×10^{-3}	69.0	45.0	73—83
Dethylaniline (43.5 ml/l) ...	0.22	0.28	2.44×10^{-3}	4.06×10^{-3}	62.4	37.5	66—76

TABLE III

ACTIVATION ENERGIES IN THE PRESENCE AND ABSENCE OF INHIBITORS

(In K-cal/mole)

Inhibitor	30 *Minutes*	60 *Minutes*	120 *Minutes*	180 *Minutes*
NIL	15.6	14.7	13.0	13.0
Methylaniline (43.5 ml/l) ...	10.14	11.52	6.45	7.37
Dimethylaniline (43.5 ml/l) ...	11.98	9.21	8.28	10.14
Ethylaniline (43.5 ml/l)	13.82	10.59	8.28	7.83
Diethylamiline (43.5 ml/l) ...	10.14	9.21	8.75	7.37

aniline in the temperature range 35°-55°C, which confirms the earlier observation regarding the beneficial effect of larger is de chain.

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 III. 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[8] 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[9] as due to an increase in surface area of metal covered by inhibitor molecules as the temperature rises. However, Riggs[10] suggested that at high coverages, the extent of absorption is no longer rate determining.

Studies of cathodic protection to aluminium-

TABLE IV

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

2.0N HC1 — Aluminium —2S — 30 minutes

Inhibitor and Inhibitor concentration	*Current density amp/cm²*	*Weight loss Mg/dm².*	*Protection current*	*%due to current inhibitor*
NIL ...	0.0	3125.0	—	—
	0.325	2829.0	9.5	—
	0.65	2566.0	17.9	—
	1.14	1971.0	36.8	—
	1.95	1054.0	66.3	—
	2.60	282.3	90.9	—
	2.76	176.9	94.3	—
	2.84	0.0	100.0	—
Methylaniline (43.5 ml/l) ...	0.0	660.0	—	78.8
	0.81	357.1	45.9	88.6
	0.89	229.1	63.3	92.7
	0.97	0.0	100.0	100.0
Dimethylaniline (43.5 ml/l) ...	0.0	701.0	—	77.6
	0.81	499.9	28.7	84.0
	0.97	219.1	68.7	93.0
	1.14	0.0	100.0	100.0
Ethylaniline (43.5 m/l) ...	0.0	482.0	—	85.1
	0.49	327.8	32.0	89.9
	0.65	165.5	65.6	94.9
	0.73	0.0	100.0	100.0
Dimethylaniline (43.5 ml/l) ...	0.0	347.3	—	89.3
	0.32	264.5	23.8	91.8
	0.41	151.0	56.5	95.3
	0.49	0.0	100.0	100.0

2S in 2.0 N hydrochloric acid indicate that addition of inhibitors considerably lowers the protective current (Table IV).

Results obtained with N-substituted aromatic amines indicate the beneficial action of longer alkylchains. Thus the protective current fro methylaniline and ethylaniline is 0.97 and 0.73 amp/cm² respectively, the corresponding values for dimethylaniline and diethylaniline being 1.1 and 0.49 amp/dm² respectively.

Results obtained under external anodic current show that the difference effect is negative for Aluminium-25 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

$$KDE = \frac{\Delta \text{ icorr}}{\Delta \text{ ipol}}$$

The values of KDE in uninhibited hydrochloric acid and in the presence of methylaniline, dimethylaniline, ethylaniline, diethylaniline are —0.37, +0.79, +0.83, +0.78 and +0.72 respectively.

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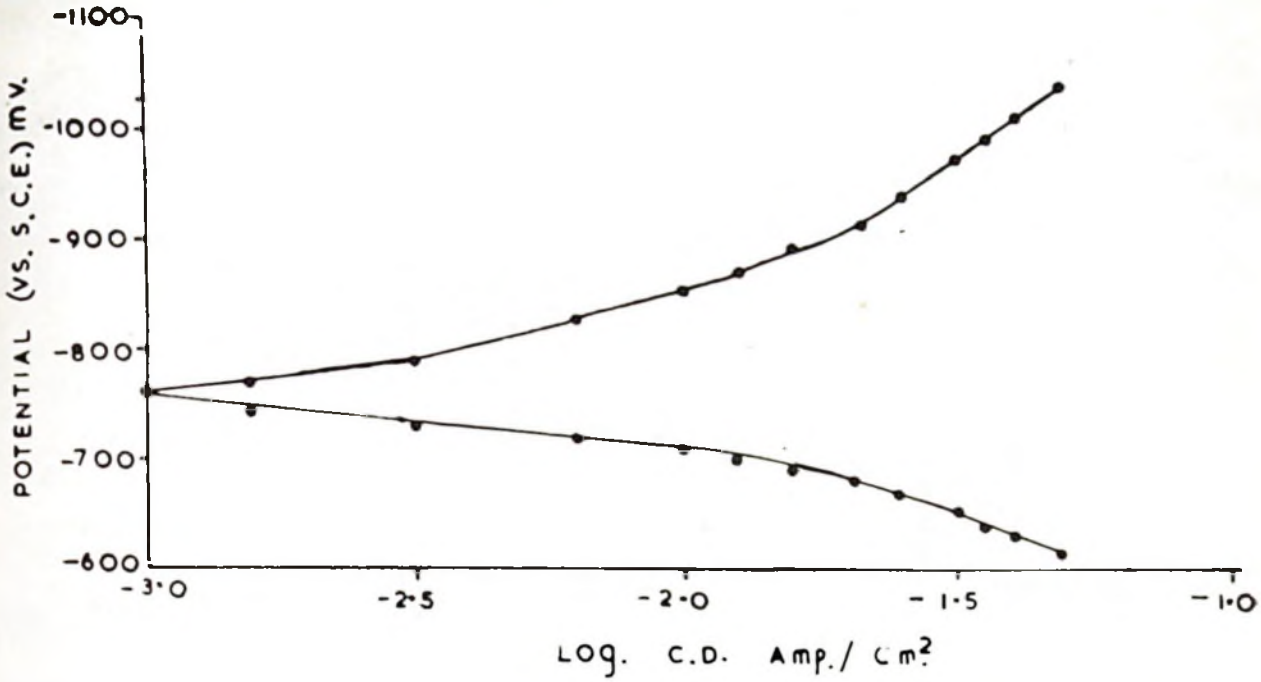


Fig. 1. Effect of varying current density on cathode and anode potentials of aluminium 2S in 1.0N hydrochloric acid.

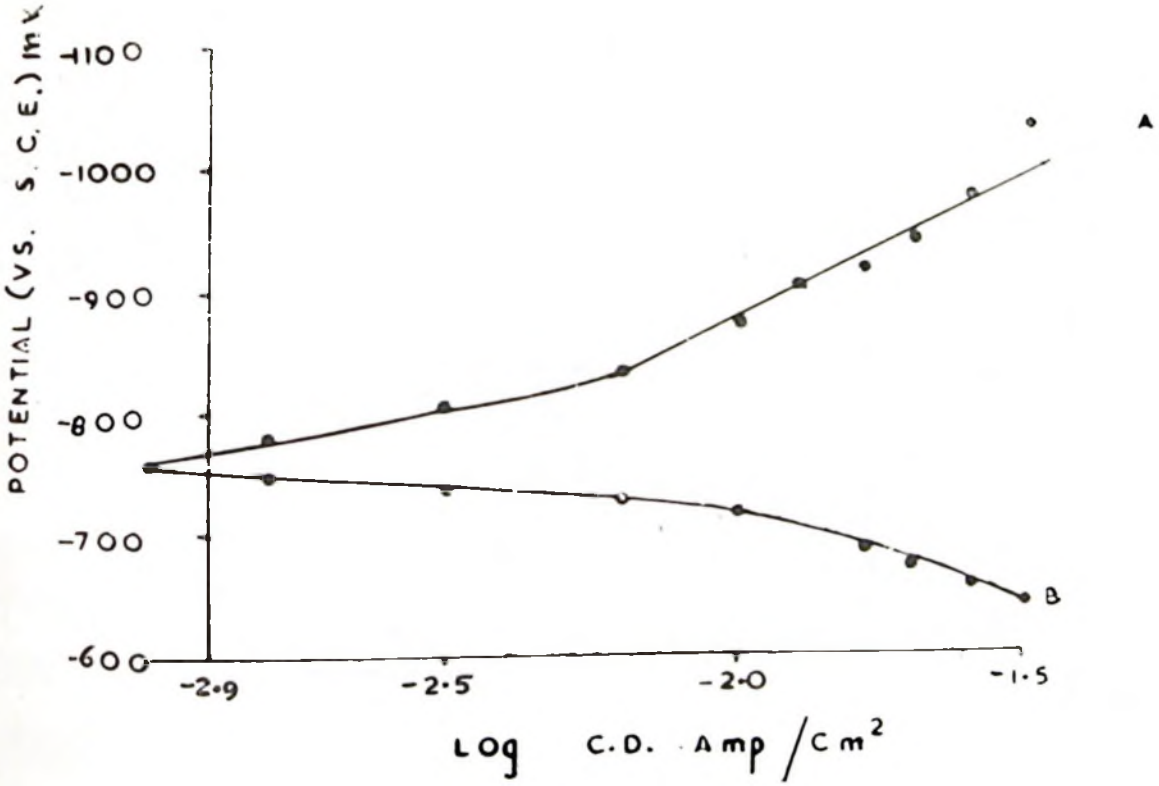


Fig. 2. Effect of varying current density on cathode and anode potentials of aluminium 2S in 1.0N hydrochloric acid in the presence of 43.5 ml./l methylaniline.

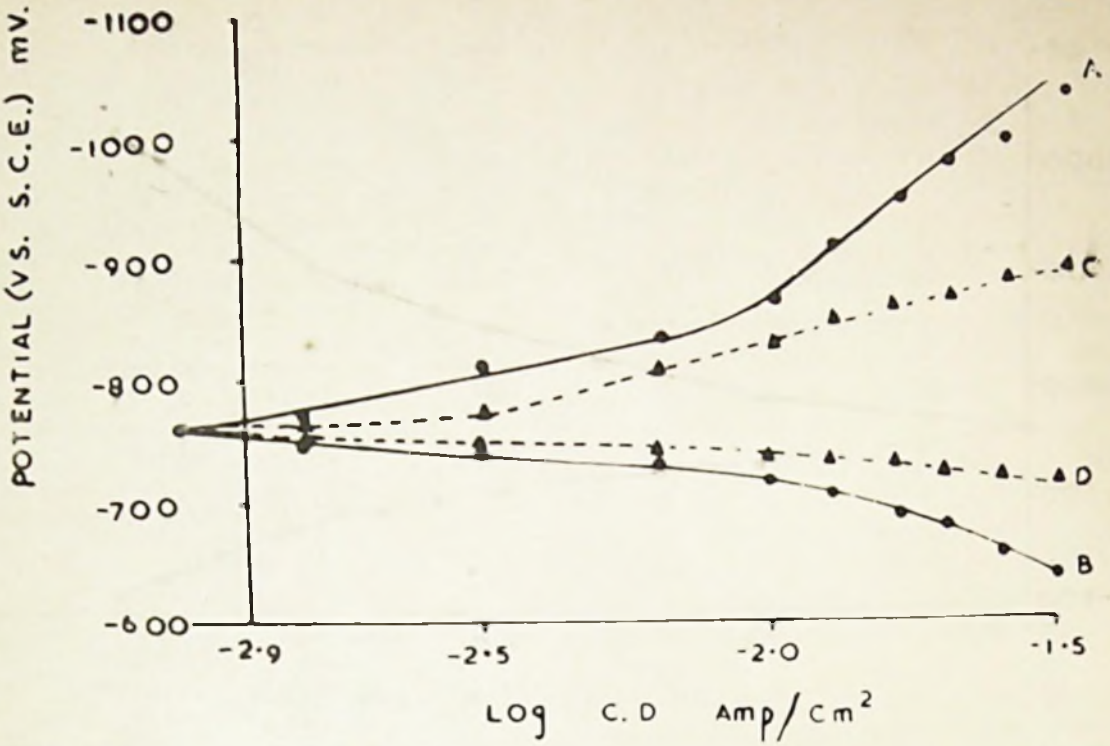


Fig. 3. Effect of varying current density on cathode and anode potentials of aluminium 2S in 1.0N hydrochloric acid in the presence of dimethylaniline
AB— 43.5 ml./l dimethylaniline
CD— 4.35 ml./l dimethylaniline

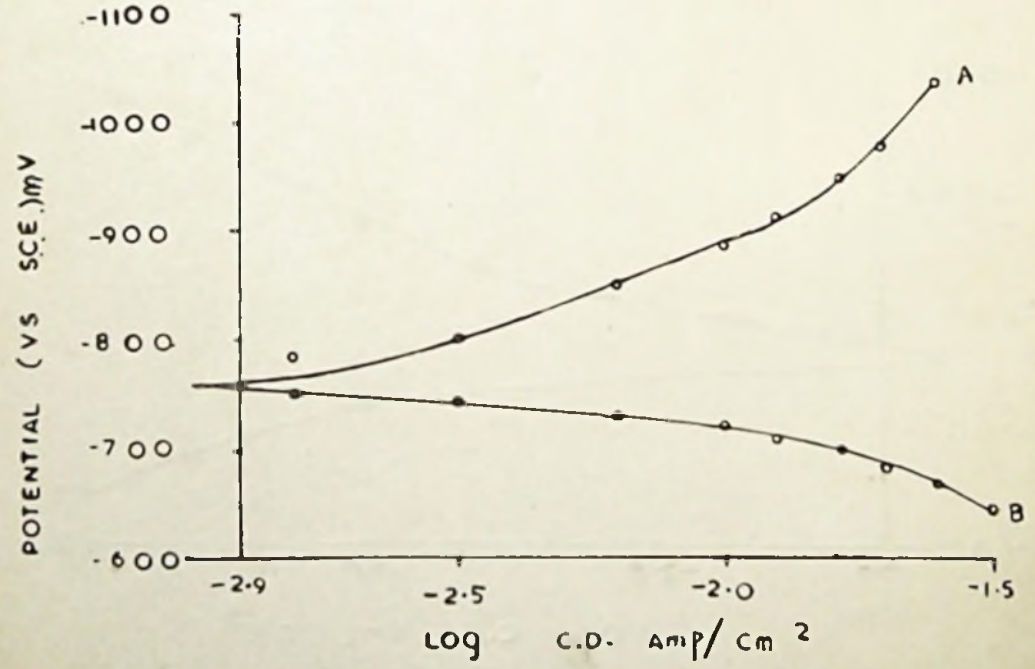


Fig. 4. Effect of varying current density on cathode and anode potentials of aluminium 2S in 1.0N hydrochloric acid in the presence of 43.5 ml./l ethylaniline.

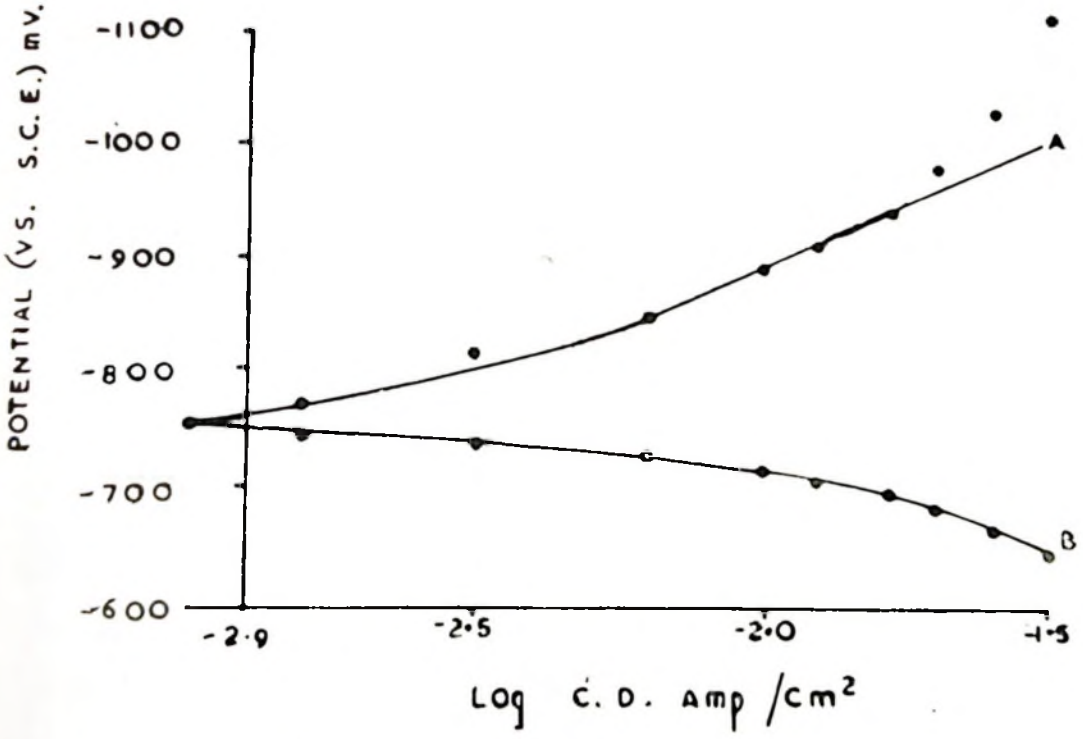


Fig. 5. Effect of varying current density on cathode and anode potentials of aluminium 2S in 1.0N hydrochloric acid in the presence of 43.5 ml./l diethylaniline.

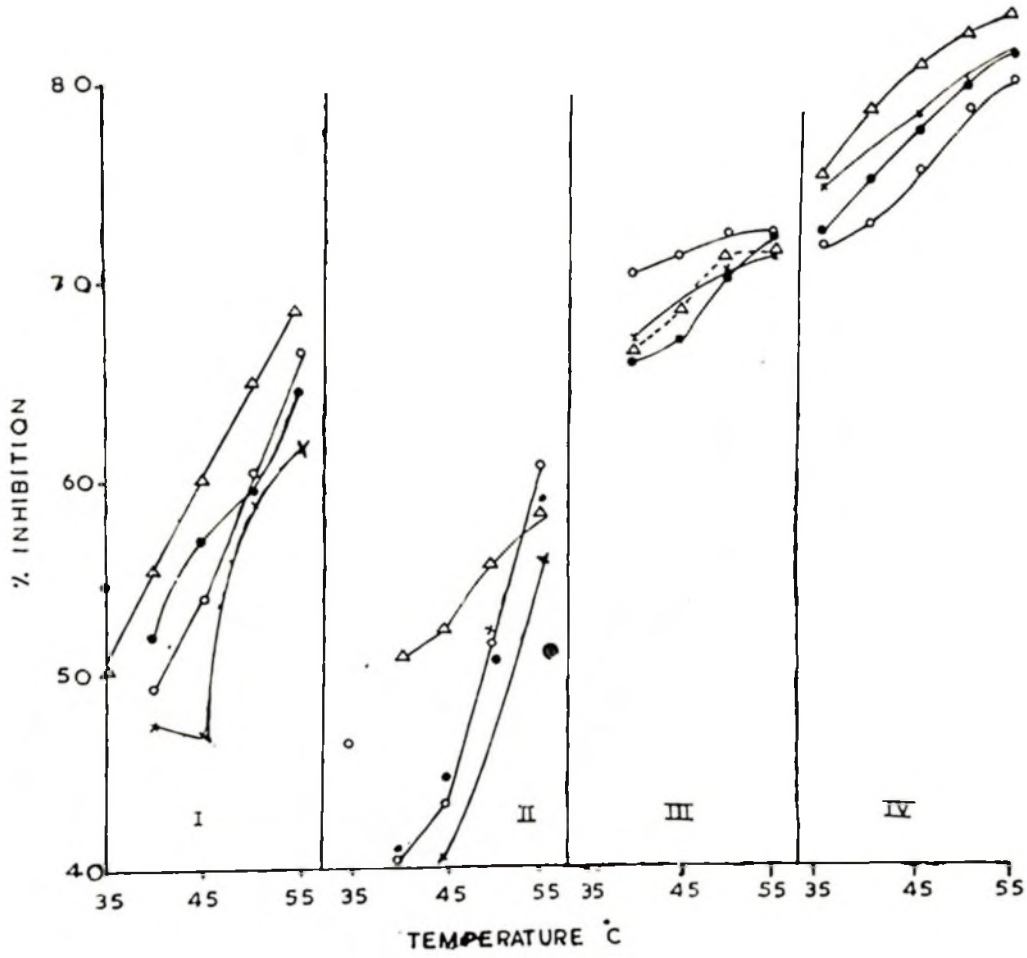


Fig. 6. Influence of temperature on the performance of inhibitors in 1.0N Hcl.