Anisidines as Corrosion Inhibitors for 3S Aluminium in Phosphoric Acid

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Inhibitor action of anisidines on the corrosion of 3S aluminium in phosphoric acid medium has been evaluated using weight loss data and polarization curves. It is found that among the anisidines, para compound is the least active and meta compound is the most active.

Phosphoric acid solutions are frequently used for cleaning aluminium, in commercial preplating, anodic oxidation and in chemical and electro-polishing of aluminium. The acid dissolves the metal to a considerable extent. It is, therfore, desirable to inhibit the solution used for pickling or to add substances like thiourea(1), glucose(2), gelatin etc. which would be helpful in reducing the etching action of the acid and also favour an increase in the brightness of the surface. Additions of substances like amines or anilines would also prove beneficial in the cleaning operations. In earlier communications, the inhibition of corrosion of 3S (Al-1.3% Mn) and B26S (Al-3.9% Cu) aluminium in solutions of phosphoric acid by some colloids(3,4), amines(5) and anilines(6,7) has been reported. In the present investigation, the role of anisidines in inhibiting the corrosion of aluminium-mangenese alloy (3S) in phosphoric acid has been reportd.

EXPERIMENTAL

Rectangular specimens (5 x 4 cm) of 3S aluminium (Supply by Indian Aluminium Co. Ltd., Bombay) were used for the determination of the corrosion rates. The percentage composition of the alloy was determined(8) and was found to be as follows:-

Mn 1.3; Fe 0.54; Si 0.65; Cu $<$0.15; Zn $\leq$0.10; Al remainder.

The preparation of specimen and the procedure for corrosion testing and cleaning were the same as described earlier (9,10). The test specimens were exposed to phosphoric acid solutions in the range 0.1 to 0.5 N, containing 0.01 to 0.5 % of anilines or anisidine at 30° ± 0.5°C unless otherwise specified.

For galvanostatic polarization studies, circular metal coupons, dia. 2.84 cm, with a handle 1.81 x 0.5 cm, were used. The area exposed to the test solution was 6.16 cm^2 ; while the applied c.d. was varied in the range 1.62 x 10^{-5} to 8.12 x 10^{-4} A/cm^2

RESULTS AND DISCUSSION

The results are given in Figs. 1-3 and Tables 1-4. The percentage inhibition, has been calculated from weight loss experiments.

Of the three stepwise dissociation of H_3PO_4 only the first one is important from the corrosion point of view. From the K values it is also apparent that solutions of phosphoric acid of pH 3 consists primarily of undissociated H_3PO_4, H^+ and $H_2PO_4^-$, and that in such solutions practically no PO_4^{3-} ions are present. As the solubilities of the different aluminium phosphates in water increase in the order:

$$AlPO_4 < Al_2(HPO_4)_3 < Al(H_2PO_4)_3 ,$$

the dissolution of aluminium in phosphoric acid may take place to a large extent through the following reaction:

$$Al + 3H_2PO_4 = Al(H_2PO_4)_3 + 3/2\ H_2$$

As a result of this reaction, which is likely to occur in pickling or anodising baths, the pH of the solution will increase and the cleaning or brightening qualities of the bath will be adversely affected. It is, therfore, desirable to add to the bath, substances which will decrease the attack on the base metal and increase the operational life of the solution.

(i) EFFECT OF INHIBITOR CONCENTRATION

Table 1 shows the effect of concentration of aniline and the three anisidines on their inhibitive efficiency. From the results, it may be generalised that the efficiency of all the inhibitors increases with increase in inhibitor concentration. The efficiency of the different inhibitors is in the order:

(a) p-anisidine < O-anisidine < aniline < m-anisidine at 0.01 - 0.05% inhibitor concentration

* Paper presented at symposeum on corrosion and its prevention, held at Varanasi on 12-13 Oct. 1984

(b) p-anisidine ∠ o-anisidine ∠ m-anisidine ∠ aniline at 0.1 - 0.5% inhibitor concentration

i.e. of the three anisidines, the meta compound is the most efficient and the para compound the least efficient inhibitor. Further a consideration of pH values shows that where solutions are required to be used at lower pH values then m-anisidine appears to be most suitable additive.

(ii) EFFECT OF ACID CONCENTRATION ON INHIBITOR EFFICIENCY

The effect of phosphoric acid concentration on inhibitor efficiency is given in Table 2. From the Table it is evident that the efficiency of all the four compounds decreases with increase in acid concentration. Further, the order efficiency of the different inhibitors in 0.1 N phosphoric acid is in the order: p-anisidine (82%) ∠ o-anisidine (92%) ∠ m-anisidine (95%) ∠ aniline (98%) but the order is p-anisidine (22%) ∠ m-anisidine (24%) ∠ o-anisidine (26%) ∠ aniline (30%) in 0.5 N H_3PO_4.

(iii) EFFECT OF EXPOSURE PERIOD

In order to examine the effect of immersion duration on inhibitive efficiency, the extent of corrosion was measured for exposure periods of 1,2 and 3 days in 0.1 N H_3PO_4 with and without 0.05% of inhibitor. In plain acid, the corrosion loss was observed to be 65.0, 107.0 and 130.0 mg for exposure periods of 1,2 and 3 days respectively. The efficiency variation with time is presented in Fig. 1

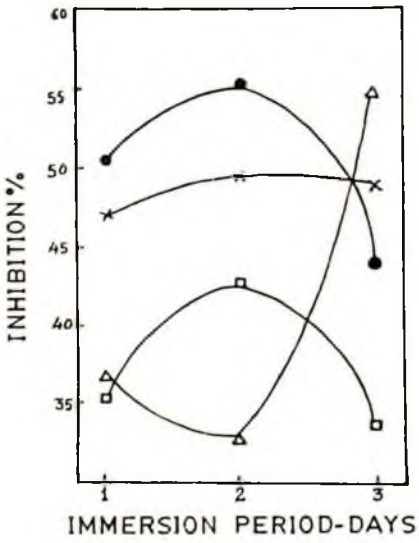


Fig.1 Effect of immersion period on inhibitor efficiency of anisidines for aluminium in 0.1 H_3PO_4 .
x–x Aniline △–△ o-anisidine
●–● m-anisidine □–□ p-anisidine

TABLE 1

EFFECT OF INHIBITOR CONCENTRATION ON INHIBITOR EFFICIENCY OF ANISIDINES FOR 3S ALUMINIUM IN 0.1N H_3PO_4

(Surface area of specimen 40 cm^2 ; Immersion period, 3 days ; Temperature 30° ± 0.5°C)

Inhibitor	pH of the medium+	Percentage inhibitor* concentration % of 0.01	0.05	0.1	0.2	0.5
Aniline	3.55	47.3	50.8	59.0	75.6	98.2
o-anisidine	2.70	42.9	46.1	52.6	59.1	91.6
m-anisidine	2.95	47.8	56.1	57.9	70.9	95.1
p-anisidine	2.40	37.8	38.6	42.5	54.8	84.4

\+ 0.1N acid + 0.5% inhibitor.

* Calculated on the basis of a blank weight loss of 114.8 mg in 0.1N H_3PO_4 . (pH = 1.5)

TABLE 2

EFFECT OF ACID CONCENTRATION ON INHIBITOR EFFICIENCY OF ANISIDINES FOR 3S ALUMINIUM IN H_3PO_4

(Specimen size, 40 cm^2 ; Inhibitor conc. 0.5% (v/v) ; Temperature 30° ± 0.5°C ; Immersion period : 3 days.)

Inhibitor	% inhibition in acid concentration of 0.1 N	0.2 N	0.3 N	0.4 N	0.5 N
Nil	(114.8)*	(130.0)	(177.0)	(235.0)	(276.0)
Aniline	98.3	48.8	27.1	29.4	29.6
o-anisidine	91.7	50.5	38.0	32.5	26.0
m-anisidine	95.2	44.5	33.1	29.2	24.0
p-anisidine	82.4	33.5	28.3	24.3	22.0

* Values in brackets show weight loss (mg) in plain acid.

(iv) EFFECT OF TEMPERATURE ON INHIBITOR EFFICIENCY

To determine the effect of temperature on inhibitive efficiency, weight losses were determined in 0.1 N H_3PO_4 with or without 0.5% inhibitor at solution temperatures of 25° 30° and 35°C. The inhibitive efficienices are given in Table 3. From the table it is evident that in the range 25°-35°C, aniline confers ~ 98% protection and its efficiency remains almost constant whereas that of o-, m- and p- anisidine slightly decreases with a rise in temperature. In general the order of increase in efficiency is found to be :

p-anisidine < o-anisidine < m-anisidine < aniline

The values of energy of activation E, were caluculated from weight loss data with the help of the equation:-

$$\log \frac{\rho_2}{\rho_1} = \frac{E}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where ρ_1 and ρ_2 are the corrosion rates (mg/dm/72h), at temperatures T_1 and T_2 (K) respectively and R the gas constant. The E values were also calculated from the slope of the plot of log ρ vs 1/T (Fig. 2) and are given in Table 3. From the table it is evident that a rise in temperature does not have much effect on the corrosion rate of aluminium in uninhibited phosphoric acid and the energy of activation is

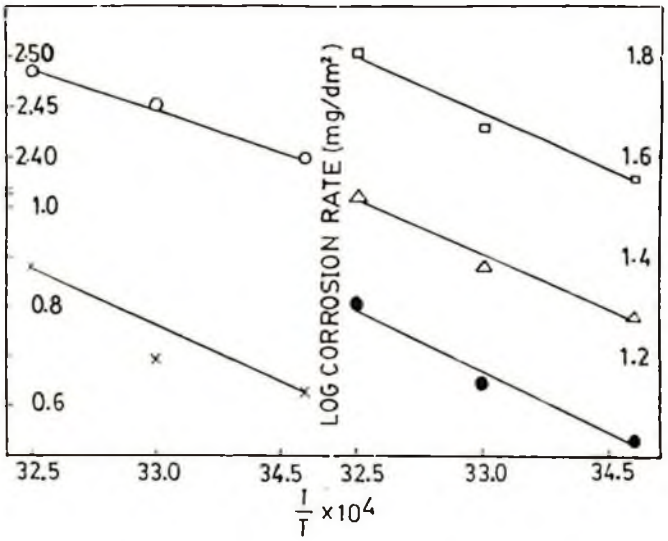


Fig. 2 Arrhenious plots for corrosion of 3S aluminium in uninhibited and inhibited (with 0.5% anisidines) 0.1 N H_3PO_4 .

o—o 0.1 n H_3PO_4 x—x aniline
Δ—Δ o-anisidine ●—● m-anisidine
□—□ p-anisidine

TABLE 3

EFFECT OF TEMPERATURE ON INHIBITIVE EFFICIENCY, VALUES OF ENERGY OF ACTIVATION (E) AND HEAT OF ADSORPTION (Q_{ads}) FOR CORROSION OF 3S ALUMINIUM IN 0.1 N H_3PO_4 CONTAINING ANISIDINES

(Specimen size, 40 cm^2 ; Inhibitor conc 0.5% , Immersion period, 3 days)

Inhibitor	% inhibition at 25°C	30°C	35°C	E from graph kcal/mole	Q_{ads}, kcal/mole, for the range 25-30°C	30-35°C
Nil	(105.0)*	(114.8)	(124.0)	3.6	-	-
Aniline	98.4 (1.7)	98.2 (2.0)	98.1 (3.1)	12.5	33.2	16.5
o-anisidine	92.4 (7.8)	91.5 (9.5)	88.7 (14.0)	9.2	22.4	16.6
m-anisidine	95.8 (4.4)	95.1 (5.5)	93.4 (8.2)	13.8	26.5	18.2
p-anisidine	85.4	84.4	78.6	12.5	16.2	17.5

* Values in brackets show weight loss (mg).

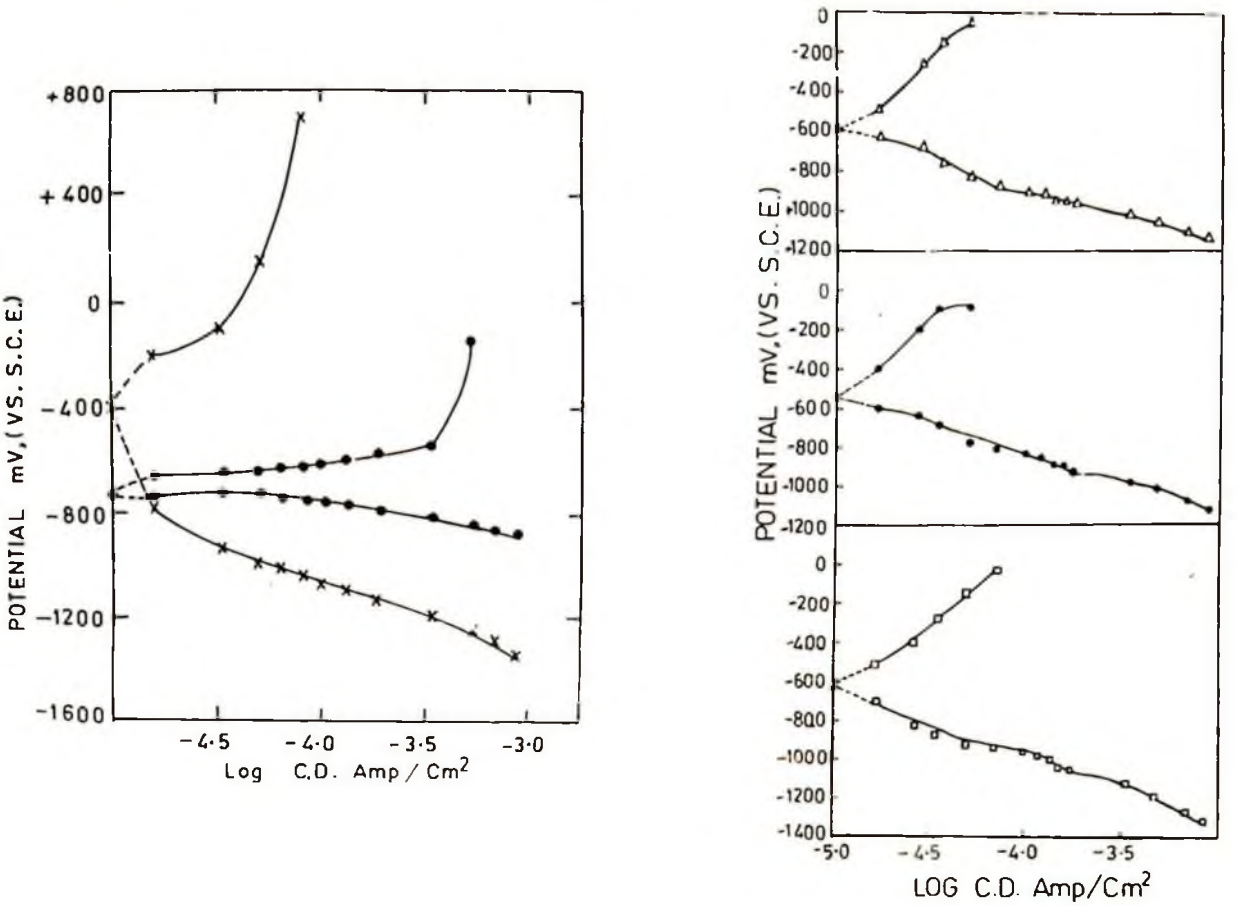


Fig. 3 Effect of C.D. on cathodic and anodic polarization of 3S Al in 0.1 H_3PO_4 in presence and absence of inhibitors.

●—● 0.1N H_3PO_4, x—x aniline Δ—Δ o-anisidine ●—● m-anisidine □—□ p-anisidine

TABLE 4

TAFEL PARAMERTERS AND INHIBITOR EFFICIENCES FOR 3S ALUMINIUM IN 0.1 N PHOSPHORIC ACID.
(INHIBITOR CONCENTRATION 0.5%)

Inhibitors	Open circuit potential(mV)	Tafel slope (V/decade)		Corrosion current from		Inhibitor efficiency (%) calculated from		Weight loss data
		Anodic	Cathodic	Intersection of cathodic and anodic Tafel lines $A/cm^2 \times 10^{-6}$ (a)	Extrapolation of cathodic Tafel line $A/cm^2 \times 10^{-8}$ (b)	(a)	(b)	
Nil	-740	0.33	0.20	35.5	79.40	-	-	-
Aniline	-330	0.32	0.27	2.75	4.47	92.2	94.4	92.2
o-anisidine	-580	0.60	0.25	5.62	8.91	84.2	88.8	91.5
m-anisidine	-560	0.66	0.25	4.27	5.01	89.0	93.7	95.1
p-anisidine	-600	0.50	0.27	6.76	14.13	81.0	82.2	84.4

quite small value, viz. $\sim$ 3.2 to kcal/mole. The higher E values in inhibited acid suggests that like unstable catalyst poisons, the adsorption of these inhibitors falls off appreciably with temperature(12). This may lead to a rise in the reaction rate as greater area of the metal is exposed to the corrosive medium.

The values of heat of adsorption were calculated with the help of the equation:

$$Q = 4{,}576 \left(\log \frac{\theta_2 / (1 - \theta_2)}{\theta_1 / (1 - \theta_1)} \right) \left(\frac{T_1 \quad T_2}{T_2 - T_1} \right)$$

and are given in Table 3. From the table it is evident that in genral, for all the inhibitors, the Q values are constant and range from 16.5 to 18.2 kcal/mole in the range 30-35°C.

(v) POLARIZATION BEHAVIOUR

A specimen of 3 S aluminium when immersed in 0.1 N H_3PO_4 develops a corrosion potential of -740 mV vs SCE. In the presence of 0.5% inhibitors the steady potentials become less negative and range from -330 mV (aniline) to -600 mV (p-anisidine). The polarization behaviour under galvanostatic conditions at different current densities in presence and absence of inhibitors is shown in Fig. 3(a) and 3(b). The plots show that in absence of the inhibitor, the anode is polarised to a greater extent than the cathode. Maximum polarization is observed in the case of aniline followed by O-, m- and p- anisidine. The inhibitor efficiencies calculated from corrosion currents obtained from the Tafel plots are found to be almost the same as those from weight loss data (Table 4).

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