INHIBITIVE ACTION OF SOME PARA-SUBSTITUTED AROMATIC AMINES TOWARDS CORROSION OF 1060 ALUMINIUM IN NITRIC ACID SOLUTION

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Some para-substituted aromatic amines have been investigated as corrosion inhibitors for 1060 aluminium in nitric acid. An effort has been made to correlate inhibitor efficiency with their structures. The efficiency of the inhibitors has been studied by weight loss method and by galvanostatic technique. It has been found that the efficiency of the inhibitors is maximum in the range of 20 to 40% nitric acid (by wt.).

Corrosion of aluminum due to nitric acid is much less at very high and low concentrations, but it is appreciably corrosive towards this metal at a concentration range of 5-60%. Considerable efforts have previously been made to find suitable inhibitors for aluminum alloys, but this system has not been studied, especially in the above mentioned concentration range. Amines have been investigated as corrosion inhibitors by many workers in different metals and systems[1–7]. In the present investigation, some para-substituted aromatic amines have been studied as corrosion inhibitors for 1060 aluminum in nitric acid both by weight loss and galvanostatic methods.

EXPERIMENTAL

The aluminium sheets (S.W.G. 24) were supplied by Hindustan Aluminium Corporation, Renukoot, Mirzapur. Preparation, testing and cleaning processes for specimens were as described by Champion[8] In weight loss experiments, specimens of size 7.5 × 5 cms were fully immersed in 300 ml of test solutions. All the solutions were prepared in double distilled water. The reproducibility of the results of weight loss experiment was within ±2%. For galvanostatic studies the specimens had a working area of 2 cm^2 with a short tag for making the electrical connections The length of the tag of the specimen was 4 cm and its surface was coated with paraffin wax. Galvanostatic experiments were carried out with 100 ml test solutions in pyrex glass cell. The external current was supplied from a lead accumulator and a set of dial type resistances were used in series for regulating the current. The potential measurements were made by a precision potentiometer (Osaw make). The null point was detected by a spot reflecting galvanometer. The procedure adopted was described by Gatos[9]. All the experiments were performed in an electronically controlled air thermostat at a constant temperature of 35° ±0.2°C. For the polarization studies, the concentration of the inhibitors used was that at which maximum inhibition was observed in weight loss experiments.

First of all, the corrosion rate of 1060 Aluminium was found by weight loss method at different concentra ions of nitric acid without any inhibitor; then the effect of the concentration of different inhibitors on the corrosion rate was found out. For this purpose, the percentage concentrations of the inhibitors chosen were 0.01, 0.1, 0.2, 0.5 and 1.0 (by wt.). Experiments were then performed to find the effect of different concentrations of nitric acid on the inhibitory action of different amines at their most effective concentrations.

RESULTS AND DISCUSSION

Results obtained in weight loss and galvanostatic experiments are summarized in the tables I and III. The percentage efficiency was calculated by the relation $\frac{I_a - I_b}{I_a} \times 100$ for galvanostatic studies. Where I_a & I_b are the corrosion currents without and with inhibitors respectively.

The corrosion rate of 1060 Aluminium in nitric acid at 35°C is maximum at a concentration of 40% by weight. From the data given in table I, it is clear that the efficiency of the inhibitors is maximum at a concentration of 0.2% except for para-amino benzoic acid for which the most effective concentration is 0.1%. Fig. 1 shows that the % efficiency of the inhibitors is maximum in 20-40% HNO_3 range except para-amino benzoic acid where the maximum efficiency is obtained at about 20% nitric acid.

Mann[10] suggested that inhibitor forms an ionizable salt with the acids. When the metals are exposed to acids, an Helmholtz double layer is formed with cations and anions on the surface of the metals. Thus

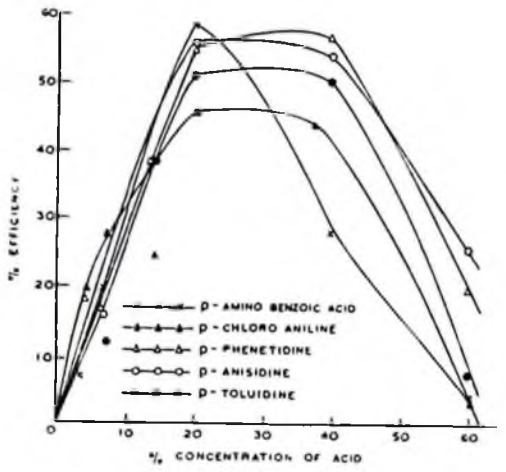


Fig. 1 Variation of % Inhibitor Efficiency with Concentration of Nitric Acid.

Table I Effect of inhibitor conc. on inhibition efficiency in 14% HNO_3 at 35 $\pm$0.2°C. Duration 48 hours.

Inhibitors & % conc.	wt. loss (mg)	% Efficiency
1. Para-Toluidine		
0.0	473	—
0.01	370	23
0.1	374	21
0.2	303	36
0.5	405	14
1.0	401	15
2. Para-Anisidine		
0.01	316	33
0.1	304	36
0.2	301	36
0.5	409	13
1.0	352	25
3. Para-Chloro aniline		
0.01	432	8
0.1	359	24
0.2	355	24
0.5	375	21
1.0	374	21
4. Para Amino Benzoic Acid		
0.01	360	24
0.1	253	47
0.2	275	42
0.5	334	29
1.0	325	31
5. Para-phenetidine		
0.01	340	28
0.1	317	33
0.2	294	38
0.5	410	13
1.0	407	14

Table-II Effect of Nitric Acid conc. on Inhibitor efficiency. Temp. 35 $\pm$0.2°C. ; Duration 48 hours.

Inhibitors & % acid conc	Loss (mg)	% Efficiency
1. Para-Toluidine		
$3\frac{1}{2}$	262	—17
7	339	12
20	306	51
40	365	50
60	433	8
2. Para-Anisidine		
$3\frac{1}{2}$	238	—7
7	320	16
20	263	56
40	339	54
60	348	26
3. Para-Chloro aniline		
$3\frac{1}{2}$	178	20
7	271	28
20	332	46
40	415	44
60	452	4
4. Para-Amino Benzoic Acid		
$3\frac{1}{2}$	208	7
7	318	20
20	260	58
40	526	28
60	452	4
5. Para-Phenetidine		
$3\frac{1}{2}$	182	18
7	320	16
20	274	55
40	315	57
60	370	20

inhibitor cations get absorbed on the cathodic sites of the metal and the surface is protected as this layer is resistant for the penetration of hydrogen ions. The positive charge of the inhibitor cations is concentrated in the nitrogen atom. The strength of the force of the adsorption of these ions on metal surface determines

the effectiveness of the inhibitors. In the case of these amines in nitric acid aluminium system, the film is adsorbed very weakly on the surface as these species are removed very easily from the surface.

Some authors have claimed that inhibitors are effective for corrosion protection due to a tendency to increase overvoltage of proton discharge process on the cathode[11–12].

In order to assess the effect of the different substigroups in aniline at para-position on the efficiency of the inhibitor, the following amines were studied, paraamino benzoic acid, para-anisidine, para-phenetidine,para-toluidine, para-chloroaniline.

The results of galvanostatic studies are shown in table III. There is very good agreement between the results obtained by weight loss method and galvanostatic technique. Fig. 2 shows a plot of potential vs. log i when anodic and cathodic polarization was done in 20% nitric acid containing 0.1% para-amino benzoic acid and without any inhibitor. Similar type of plots were obtained for other inhibitors also. In all the cases it has been found that both cathode and anode are polarized. Fig. 3 shows the variation of potential with time in presence and absence of the inhibitors in 14 per cent nitric acid. In all the cases, the potential values with time are more negative than those in absence of the inhibitors indicating the action of the inhibitors on the local cathodes.

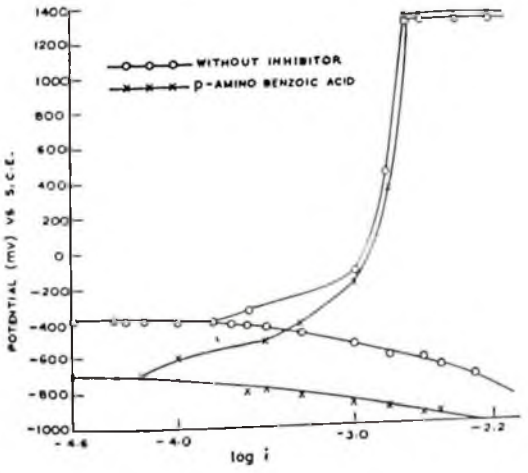


Fig. 2 Effect of Current Density on the Cathodic and Anodic Potential.

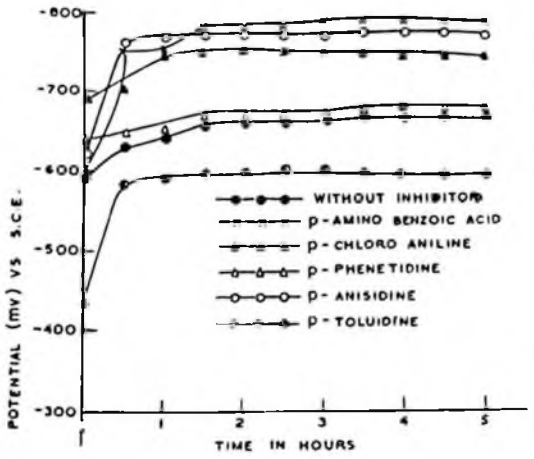


Fig. 3 Variation of Potential with Time in 14% Nitric Acid,

pK_a or pK_b value is also given in table III. It is clear that para-amino benzoic acid shows maximum efficiency and the efficiency decreases in the following order :

para-amino benzoic acid> para-anisidine> para-phenetidine> para-toluidine> para-chloro aniline.

Riggs[13–14] et al have also suggested that if the electron acception characteristics of aniline could be improved by the addition of a group to the ring which could stabilize the electron accepting characteristic of the amino group, the inhibitive character of the resultant compound would increase. This is found in agreement with our results. Electron releasing capacity of the substituent group at para-position goes on decreasing from -COOH group to-Cl group in the above mentioned order. It is also interesting to note that pK_a value for para-amino benzoic acid is 4.92 which shows maximum efficiency. As the pK_b value for other amines increases the efficiency decreases. Therefore, the basic character of the amines is also an indication towards its efficiency.

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Table-III Comparison Efficiencies Calculated by Weight Loss Method and by Galvanostatic Technique in 20% Nitric Acid.

Inhibitors	pK_a[15] or pK_b values	Corrosion current Amp/cm²	Cathodic Tafel slopes V/dec.	% Efficiencies calculated by	
				Wt. loss method	By intersecting Tafel lines
Without Inhibitors	—	0.166×10^{-3}	0.076	—	—
Para-Amino Benzoic Acid	4.92*	0.691×10^{-4}	0.228	58	58
Para-Anisidine	8.71	0.691×10^{-4}	0.218	56	58
Para-phenetidine	8.70	0.691×10^{-4}	0.178	55	58
Para-Toluidine	8.93	0.796×10^{-4}	0.212	51	52
Para-Chloro-aniline	10.19	0.871×10^{-4}	0.108	46	47

*pK_a value

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