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Effect of Nitro Group on Inhibition of 1070 Aluminium by Benzoic Acid in Nitric Acid

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Corrosion inhibition action of *o*-, *m*- and *p*-nitrobenzoic acid has been thoroughly studied at 30, 40 and 50°C using weight loss and potentiostatic techniques. Inhibition efficiency of nitrobenzoic acids increases with concentrations but decreases with rise in temperatures. It has been found that nitro group exhibits beneficial effect on the inhibitive efficiency of the inhibitors. In case of all the inibitors maximum inhibition efficiency has been observed at 0.5% concentration. Lower value of activation energy and heat of adsorption have been obtained at higher temperatures. Polarisation studies reveal that these compounds act as mixed inhibitors.

INTRODUCTION

Several organic inhibitors have been used to prevent the corrosion of aluminium and its alloys in nitric acid[1–6]. Some of the aromatic acids and compounds containing hydroxy group have also been used for the protection of metallic corrosion in different corrosive media[7–9]. The present paper deals with the role of nitro group in the mechanism of inhibition of corrosion of 1070 aluminium in 20% nitric acid in the presence of some nitrobenzoic acids namely *o*-, *m*- and *p*-nitrobenzoic acid. This paper also throws some light on the energy of activation of the system undertaken.

EXPERIMENTAL

The chemicals used in the present investigation were of AnalaR grade except *m*-nitro benzoic acid, which was synthesised in the laboratory and its purity was ascertained by determining the sharp melting point. 1070 grade of aluminum sheets supplied by M/s. Hindalco, Renukoot, Sonbhadra (India) were used in the present work. The test solutions were prepared in double distilled water. The preparation of specimens (size 75 mm × 50 mm × 0.5 mm) and cleaning procedure were the same as described by Champion[10]. Weight loss experiments were carried out by dipping the specimens in 20% nitric acid for a period of 48 h. Inhibition

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efficiencies were evaluated for 0.01, 0.2, 0.5 and 1.0% of the inhibitors at 30, 40 and 50°C using the equation:

$$\text{Percentage inhibition efficiency} = [(a - b)/a] \times 100$$

where a = weight loss in the uninhibited solution, and

b = weight loss in the inhibited solution.

The polarisation experiments were performed at 0.5% concentration of the inhibitors at 30°C. The details of weight loss and potentiostatic, anodic and cathodic polarisation studies were the same as reported elsewhere[11].

RESULTS AND DISCUSSION

The results are given in Tables 1 and 2. It is evident from Table-1 that all the inhibitors used show maximum inhibition efficiency at a concentration of 0.5%. The inhibition efficiency of nitrobenzoic acids increases in the order: *p*-nitrobenzoic acid < *m*-nitrobenzoic acid < *o*-nitrobenzoic acid. It has been shown by Chakrabarty *et al.*[7] that benzoic acid containing —COOH group, an electron withdrawing group, inhibits corrosion of aluminium by the mechanism of adsorption through the delocalised π-electrons in the benzene ring. In case of nitrobenzoic acids two electron attracting groups, *i.e.* carboxylic group and nitro group attached to the same benzene nucleus reduce the π-electron density of the benzene ring to a greater extent. Thus they should be expected to be very poor inhibitors. But it is surprising to note that the nitrobenzoic acid is a better inhibitor than benzoic acid[7]. The above contradictory result is probably due to the adsorption of nitrobenzoic acid through lone pair of electrons of the nitrogen atom. Owing to the electron withdrawing capacity of —NO_2 group, electron density increases on nitrogen atom. As a result, the extent of adsorption enhances and, therefore, corrosion rate of 1070 aluminium decreases. The differences in the inhibitive tendency of the isomers of nitrobenzoic acid may be propounded on the basis of the following reasoning: *p*-nitrobenzoic acid is stronger than benzoic acid due to polar influence of the nitro group transmitted through the ring. The nitro group, however, behaves in the same way in the *o*-position, but the *o*-nitrobenzoic acid is a stronger acid than the *p*-isomer. It is a fact that any structural change in the molecule that will stabilise the anion will, therefore, increase the strength of acid. An *o*-nitro group can stabilise the *o*-nitrobenzoate ion by intramolecular hydrogen bonding, and therefore *o*-nitrobenzoic acid is stronger than *m*- and *p*-isomers. Thus *o*-nitro benzoate ion is formed easily. The extent of formation of anions of these isomers increases in the order of increasing behaviour of intra molecular hydrogen bonding given as: *para* < *meta* < *ortho*-nitrobenzoic acid. Hence, it may be assumed that the adsorbability of these inhibitors and inhibition efficiency should follow the trend of intramolecular hydrogen bonding.

TABLE-1
EFFECT OF TEMPERATURE AND CONCENTRATION ON THE INHIBITIVE EFFICIENCY OF NITROBENZOIC ACID FOR 1070 ALUMINIUM IN 20% NITRIC ACID

Immersion period = 48 h.

Inhibitor and percentage concentration	Percentage inhibitive efficiency at a temperature of		
	30°C	40°C	50°C
o-nitrobenzoic acid			
0.01	40	35	32
0.20	51	46	42
0.50	60	55	51
1.00	48	42	37
m-nitrobenzoic acid			
0.01	40	33	28
0.20	50	44	39
0.50	58	53	48
1.00	47	42	38
p-nitrobenzoic acid			
0.01	30	23	19
0.20	40	34	30
0.50	53	48	44
1.00	44	39	35

TABLE-2
VALUES OF ENERGY OF ACTIVATION (E_a) AND HEAT OF ADSORPTION (Q_{ads}) FOR DIFFERENT INHIBITORS FOR CORROSION OF 1070 ALUMINIUM IN 20% NITRIC ACID

Inhibitor and percentage concentration	E_a, kJ/mole, from weight loss data for the temperature range		Q_{ads}, kJ/mole, for the temperature range	
	30–40°C	40–50°C	30–40°C	40–50°C
20% Nitric acid	64.2	64.9	—	—
o-nitrobenzoic acid				
0.01	70.5	68.7	16.84	11.33
0.20	71.9	71.0	15.80	13.67
0.50	73.6	72.1	16.14	13.51
1.00	73.0	71.4	19.14	17.60
m-nitro benzoic acid				
0.01	72.9	71.0	23.88	19.86
0.20	73.2	72.1	19.01	17.34
0.50	73.3	72.7	16.00	16.84
1.00	71.3	70.6	16.00	14.01
p-nitro benzoic acid				
0.01	71.7	69.2	28.47	20.31
0.20	71.8	69.8	20.34	15.47
0.50	72.2	71.2	15.80	13.53
1.00	71.1	70.2	16.27	14.42

Energy of activation and heat of adsorption, as shown in Table-2, decrease with rise in temperature. It is further seen from this table that in 20% nitric acid activation energy increases with the increased concentration of nitrobenzoic acids and reaches a maximum value at a concentration showing maximum inhibition efficiency. On the other hand, for heat of adsorption no such behaviour is observed. Our observations are in harmony with the finding of Putilova[12] who reported that the activation energy of the process is higher in the presence of inhibitor than in the absence of it which retards corrosion at low temperature but inhibition is reduced at elevated temperatures.

Anodic as well as cathodic polarisation curves in the presence of 0.5% inhibitor are something similar to the curves reported earlier[7]. In the presence of inhibitors the cathodic polarisation curves are almost parallel to the curve observed in blank solution, *i.e.*, 20% nitric acid and all the inhibited curves have shifted towards lower region of current density. Anodic polarisation curves are affected by inhibitors and a considerable lowering in the current density in active and passive region is seen in the presence of them. The results of polarisation studies may be explained on the concept of adsorption of inhibitor molecules on the metal surface. The absorbed molecules diminish the blank surface area for anodic and cathodic reactions occurring at the metal surface. Consequently current density decreases. Thus, polarisation studies reveal the fact that all nitrobenzoic acids are mixed inhibitors and effective on both cathodic and anodic sites.

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REFERENCES

1. R.S. Chaudhary, D.D.N. Singh, P.N.S. Yadav and C.V. Agarwal, *J. Electrochem. Soc. (India)*, **28**, 169 (1979).
2. R.S. Chaudhary, D.D.N. Singh and C.V. Agarwal, *J. Electrochem. Soc. (India)*, **27**, 91 (1978).
3. D.D.N. Singh, C. Chakrabarty, R.S. Chaudhary and C.V. Agarwal, *J. Appl. Electrochem.*, **11**, 671 (1981).
4. D.D.N. Singh, R.S. Chaudhary, B. Prakash and C.V. Agarwal, *Brit. Corros. J.*, **14**, 235 (1979).
5. D.D.N. Singh, R.S. Chaudhary and C.V. Agarwal, *J. Electrochem. Soc. (India)*, **28**, 241 (1979).
6. D.D.N. Singh, M.M. Singh, R.S. Chaudhary and C.V. Agarwal, *J. Appl. Electrochem.*, **10**, 587 (1980).
7. C. Chakrabarty, M.M. Singh, P.N.S. Yadav and C.V. Agarwal, *Trans. SAEST*, **18**, 13 (1983).
8. N. Subramanyam, S. Venkatakrishna lyer and V. Kapali, *Trans. SAEST*, **15**, 251 (1980).
9. M.N. Desai and Y.C. Shah, *Works und Korr.*, **21**, 795 (1970).
10. F.A. Champion, Corrosion Testing Procedures, Champion and Hall, London, p. 187 (1952).
11. R.S. Chaudhary, P.N.S. Yadav and C.V. Agarwal, *J. Appl. Electrochem.*, **13**, 807 (1983).
12. I.K. Putilova, S.A. Balezin and V.P. Balezin, Metallic Corrosion Inhibitors (English), Pergamon Press, p. 30 (1960).

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