



Inhibition of Corrosion of Mild Steel in 10 % Sulfamic Acid by Azo Dyes

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Abstract

The inhibitive influence of 3-Nitro-4'-N,N-dimethylaminoazobenzene and 4-Nitro-4'-N,N-dimethylaminoazobenzene was studied on the corrosion of mild steel in 10 % sulfamic acid. The values of percentage inhibition efficiency by the methods, showed close agreement. The difference in inhibitive action was explained on the basis of their molecular structure. The p-isomer was found to give the higher inhibition efficiency than m-isomer. The steady OCP value for mild steel, dipped in 10 % sulfamic acid, was not considerably shifted by the increasing addition of the inhibitor. However, the corrosion of mild steel dipped in 10 % sulfuric acid was predominantly under anodic control, in the presence and in the absence of the dye. Both the anodic and the cathodic processes are polarized considerably with the increasing concentration of the inhibitor. Therefore the inhibition is of mixed type.

Keyword : Azo dyes

Introduction

The study of organic inhibitors in acid medium is an attractive field of research due to its usefulness in several industries. Most of the commercial formulations include aldehydes and amines as essential ingredients [1,2]. It is known that condensation products of carbonyls and amines, known as anils or Schiff's bases, give more inhibition efficiency than the constituent carbonyls and amines, were used as corrosion inhibitors for mild steel in hydrochloric acid [4]. Similar observations have been reported recently [5-6]. They have studied corrosion inhibiting properties of several anils, synthesized by condensing either aromatic or heterocyclic amines with aromatic aldehydes. These observations have prompted us to investigate the inhibiting behaviour of some

azo dyes, prepared by us from aromatic amines, on the corrosion of mild steel in sulfuric acid solutions.

Experimental Methods

The commercially available mild steel coupons were used in our studies. Double distilled water was prepared by distilling distilled water in all pyrex-glass unit with a few crystals of potassium permanganate and one pellet of sodium hydroxide. Chemically pure analytical grade reagents were used in the studies. Solutions were prepared in double distilled water. The inhibitors are prepared as given below.

Preparation of 3-nitro-4'-N, N-dimethyl amino azobenzene

m-Nitroaniline (0.05 mole) was dissolved in 10 ml of con. HCl and the solution was cooled in ice-cold saturated sodium

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nitrite solution (10 ml) was added slowly with stirring. Then 10 ml of N, N-dimethylaniline (0.07 mole) in dilute HCl was added slowly with stirring to get a red dye. The dye was isolated from the solution by filtration at a suction pump. It was washed with cold water and air-dried [7].

Preparation of 4-nitro -4'-N,N-dimethyl amino azobenzene

Acetanilide (0.01 mole) was dissolved in 14 ml of glacial acetic acid in a conical flask. Con. sulphuric acid (30 ml) was added very slowly, with constant shaking. The flask was cooled in a freezing mixture of crushed ice and crude common salt. Then fuming nitric acid (6 ml) was added very slowly with gentle shaking to the flask so that the temperature does not rise above 20°C. The contents of the flask were shaken vigorously for about an hour. Then, it was poured into cold water in a thin stream, slowly with shaking. The product was allowed to stand for an hour, filtered off at the pump and then washed with water. The p-nitroacetanilide (0.07 mole) was mixed with con. HCl (15 ml) in a round-bottom flask, fitted with an air-condenser and refluxed for about 40 minutes. The p-nitroaniline is liberated on neutralizing the reaction mixture with an excess of aqueous ammonia. The contents were cooled. The yellow precipitate that separates out is filtered off at the pump, washed with cold water and dried [7]. The p-nitroaniline was diazotized as described earlier.

Weight Loss Experiment

The test specimens were cut into pieces of dimension, 4 cm x 1 cm x 0.1 cm, with the help of a shearing machine and the edges were smoothed. They were abraded into uniform surfaces with the help of a grinding machine and finally polished. Then 10 ml of N, N-dimethylaniline (0.07 mole) in dilute HCl with 150, 300, 400 and 600 grades of emery papers. All specimens were washed with double distilled water and degreased with 99.2 % ethyl alcohol, dried and stored in vacuum desiccator containing silica gel.

During the study the specimens were suspended with the help of glass hooks in conical flasks containing 100 ml of 10 % sulfamic acid solution with and without the inhibitor for a specified length of time. Then these specimens were removed, rubbed with brush to remove any corrosion products, washed with water and finally washed with acetone and distilled water, dried in an oven and re-weighed. From the weight loss measurements the percentage inhibition efficiency was calculated according to the formula given below.

$$\text{Percentage Inhibition} = \frac{W_0 - W_i}{W_0} \times 100$$

Where W_0 and W_i are the weight losses without and with the inhibitor in the acid solution, respectively.

OCP Measurement

The mild steel electrode was dipped in 10 ml of 10 % sulfamic acid solution with and without the inhibitor coupling it with saturated calomel electrode (SCE) and the steady values of open circuit potential (OCP) were measured.

Mild Steel / 10 % sulfamic acid + dye SCE

Polarisation Studies

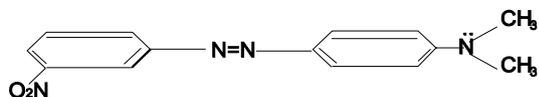
For electrochemical polarization studies, flag shaped metal specimens, with sufficiently long tail, were cut from the mild sheet leaving a working area of 1 cm² on one side of the specimen and a small portion at the tip of the tail for providing electrical contact, rest of the surface was coated with enamel lacquer. The electrochemical investigations were carried out in a three electrode cell with the platinum electrode as the counter electrode, a standard calomel electrode as the reference electrode and the mild steel electrode as the working electrode.

After measuring OCP value, the mild steel electrode was polarized cathodically by passing known values of current in the increasing steps of 10 mA min⁻¹ and the steady potential was measured at each current density.

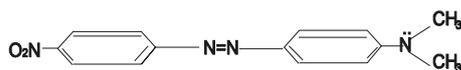
After cathodic polarisation was over the working electrode was brought back to the OCP and then polarised anodically as explained above. The corrosion current I_{corr} and corrosion potential E_{corr} were evaluated by the extrapolation of the cathodic and anodic Tafel plots.

Results and Discussion

The scale deposits are formed on the metal surface of heat exchangers, evaporators, vacuum pans and crystallisers in industries. These deposits consists of a mixture of silicates and carbonates of calcium and magnesium. The descaling operation is carried out with sulfamic acid because it is a non-fuming substance, less corrosive to metals than mineral acids and readily removes silica deposits. Literature survey reveals that use of organic corrosion inhibitors in sulfamic acid media are sparse and therefore we carried out the study of the inhibition of corrosion of steel in sulfamic acid media. The azo dyes used as inhibitors are shown below.



3 – nitro - 4' - N, N-dimethylaminoazobenzene



4 – nitro - 4' - N, N-dimethylaminoazobenzene

The values of corrosion rate and inhibition efficiency (IE) obtained from weight loss measurements for different concentrations of each of the inhibitor in 10 % sulfamic acid are shown (Table 1 & 2). It was evident that the inhibition efficiency increased as the concentration of inhibitor increased and the optimum concentration of inhibitor under investigation required to achieve the maximum inhibition was found to be 10×10^{-5} M. The increase in the concentration of inhibitor probably leads to a greater surface coverage resulting in further decrease in the corrosion.

Table 1. Effect of 3-Nitro-4'-N,N-dimethylaminoazobenzene on the rate of corrosion of mild steel in 10% sulfamic acid at $\pm 30^\circ\text{C}$

[DYE] x $10^5, \text{M}$	Rate of corrosion $\times 10^4, \text{g cm}^{-2} \text{h}^{-1}$	Percentage inhibition
Nil	1.63	-
1.0	1.56	14.1
2.0	1.49	18.0
3.0	1.10	27.1
4.0	1.07	37.5
5.0	0.92	47.6
6.0	0.76	51.0
7.0	0.68	56.0
8.0	0.56	63.8
9.0	0.49	71.4
10.0	0.49	71.4
11.0	0.49	71.4

The difference in inhibitive action was explained on the basis of their molecular structure. The p-isomer was found to give the highest inhibition efficiency. This can be explained on the basis of the presence of resonance interaction between the p-nitro and p-N,N-dimethylamino groups in the isomer. The

extensively delocalised pi-electron favours greater adsorption on the metal surface, thereby giving rise to high values of inhibition efficiency i.e. 80.4% at a concentration of 10×10^{-5} M. Such interaction is not possible in meta-isomer.

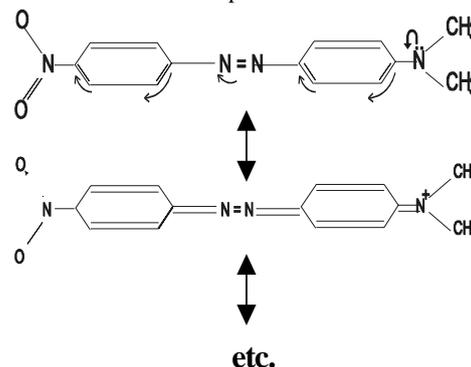


Table 2. Effect of 4-Nitro-4'-N,N-dimethylaminoazobenzene on the rate of corrosion of mild steel in 10% sulfamic acid at $\pm 30^\circ\text{C}$

[DYE] x $10^5, \text{M}$	Rate of corrosion $\times 10^4, \text{g cm}^{-2} \text{h}^{-1}$	Percentage inhibition
Nil	1.56	-
1.0	1.28	26.3
2.0	1.22	45.6
3.0	0.84	57.7
4.0	0.66	62.1
5.0	0.59	62.1
6.0	0.50	67.7
7.0	0.44	71.3
8.0	0.35	77.2
9.0	0.32	78.1
10.0	0.32	80.4
11.0	0.32	80.4

The extent of adsorption depends, on the intensities of pi-electron cloud in the phenyl ring [8]. In the case of meta-isomer (3-nitro-4'-N,N-dimethylaminoazobenzene), it was observed that the colour of the dye disappeared due to corrosion reactions. This may be due to the reduction of the azo compound. Hydrogen arising from the corrosion reaction is probably responsible for the reduction of the dye[9].

The OCP shifted towards positive direction in the presence of inhibitor, indicating that the inhibitor acts as an anodic inhibitor. But the shift in OCP is small suggesting that complete polarization curve should be considered to confirm whether the inhibition is cathodic or anodic or of mixed type. The cathodic and the anodic polarisation curves are

Table 3. Anodic and cathodic polarization of mild steel in 10 % sulfamic acid without & with 3-Nitro-4'-N, N-dimethylaminoazobenzene

[DYE] x 10 ⁵ ,M	OCP, V	E _{corr.} , V	b _c , volt/dec	b _a , volt/dec	I _{corr.} , mA cm ⁻²	Percentage inhibition
Nil	0.49	0.50	0.210	0.924	0.44	-
1.0	0.49	0.49	0.245	0.902	0.36	18.0
2.0	0.47	0.47	0.245	0.902	0.34	22.7
3.0	0.48	0.46	0.256	0.911	0.27	38.6
4.0	0.48	0.47	0.259	0.902	0.25	43.1
5.0	0.49	0.49	0.245	0.902	0.21	52.2
6.0	0.48	0.49	0.245	0.902	0.20	54.5
7.0	0.49	0.48	0.245	0.902	0.16	63.6
8.0	0.48	0.48	0.245	0.935	0.14	68.0
9.0	0.49	0.48	0.196	0.935	0.13	70.4
10.0	0.49	0.48	0.245	0.920	0.12	72.0
11.0	0.49	0.48	0.259	0.935	0.13	70.4

Table 4. Anodic and cathodic polarization of mild steel in 10 % sulfamic acid without & with 3-Nitro-4'-N, N-dimethylaminoazobenzene

[DYE] x 10 ⁵ ,M	OCP V	E _{corr.} , V	b _c , volt/dec	b _a , volt/dec	I _{corr.} , mA cm ⁻²	Percentage inhibition
Nil	0.49	0.50	0.210	0.924	0.44	-
1.0	0.49	0.49	0.245	0.902	0.36	18.0
2.0	0.47	0.47	0.245	0.902	0.34	22.7
3.0	0.48	0.46	0.256	0.911	0.27	38.6
4.0	0.48	0.47	0.259	0.935	0.25	43.1
5.0	0.49	0.49	0.245	0.902	0.21	52.2
6.0	0.48	0.49	0.245	0.902	0.20	54.5
7.0	0.49	0.48	0.245	0.902	0.16	63.6
8.0	0.48	0.48	0.245	0.935	0.13	70.4
9.0	0.49	0.48	0.196	0.935	0.11	75.0
10.0	0.49	0.48	0.245	0.902	0.09	79.5
11.0	0.49	0.48	0.295	0.902	0.05	81.1

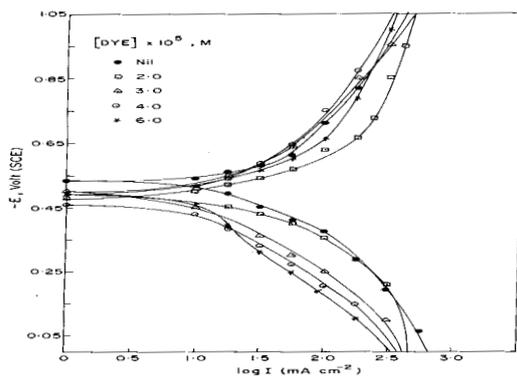


Fig. 1. Anodic and Cathodic Polarisation of Mild Steel in 10% Sulfamic Acid without and with 3-nitro-4'-N,N-dimethylaminoazobenzene

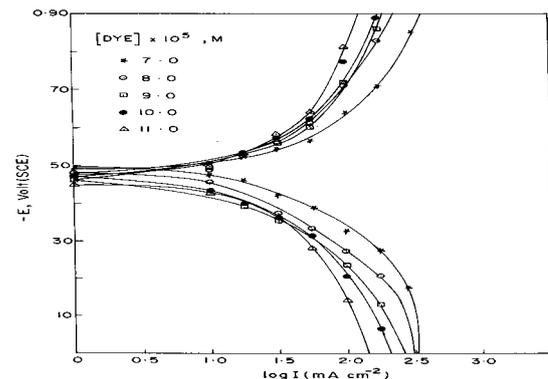


Fig. 2. Anodic and cathodic Polarisation of mild steel in 10% sulfamic acid without and with 3-nitro-4'-N,N-dimethylaminoazobenzene

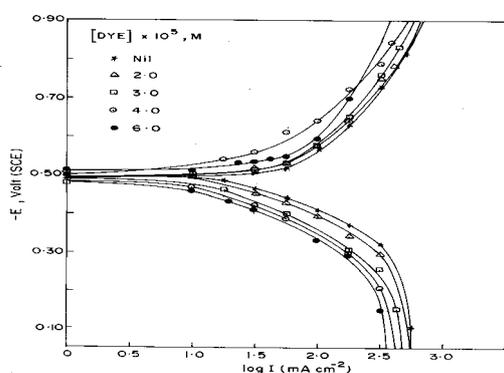


Fig. 3. Anodic and cathodic Polarisation of mild steel in 10% sulfamic acid without and with 4 - nitro - 4' - N₁N₁-dimethylaminoazobenzene

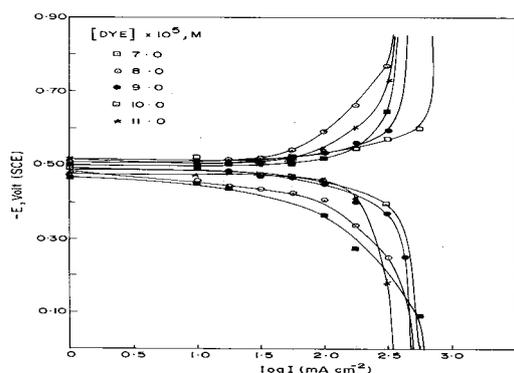


Fig.4. Anodic and cathodic polarization of mild steel in 10% sulfamic acid without and with 4-nitro - 4' - N₁N₁-dimethylaminoazobenzene

shifted towards lower current density values in the presence of inhibitor. This observation indicates that the inhibitor suppresses both anodic as well as cathodic reactions. A decrease in the corrosion current and increase in the anode Tafel slope values have been observed with the increase in the concentration of inhibitor [10]. The parallel anodic and cathodic polarization curves show that decrease in corrosion current is observed due to the simple blocking effect of inhibitor adsorbed on the metal surface, which in turn decreases the dissolution reaction rate [11]. No passivation is observed at any concentration of the inhibitor.

The addition of these dyes to the acid solution did not cause any significant change in the values of E_{corr} . Thus they inhibit corrosion of mild steel in acid solution by blocking the active sites of steel surface [12,13]. Since both the anodic and the cathodic processes are polarised considerably with the

increasing concentration of inhibitor, inhibition is of mixed type.

Conclusion

The inhibitor, 4-Nitro-4'-N,N-dimethylaminoazobenzene is found to inhibit more effectively the corrosion of mild steel in 10 % sulfamic acid than the corresponding 3-nitro isomer, possibly due to the resonance interaction between the pi-electron clouds of 4-nitro and 4'-N,N-dimethylamino groups.

Both inhibitors appear to inhibit corrosion of mild steel by suppressing both the anodic and cathodic processes involved in corrosion by physically blocking the metal surface.

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