Inhibition Of Corrosion Of Mild Steel In Hydrochloric Acid By Some Azo Dyes

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ABSTRACT

The effect of metanil yellow, Naphthol blue black and solochrome dark blue azo dyes on the corrosion behaviour of mild steel in hydrochloric acid is reported at 30°C and 40°C using weight loss technique. The study reveals that metanil yellow gives a higher inhibition efficiency than solochrome dark blue while naphthol blue black is the least inhibitive. The inhibitive effect is more pronounced with increasing temperature as well as inhibitor concentration. The mechanism of chemical adsorption has been proposed for the three inhibitors. The difference in the inhibiting properties of the three inhibitors is explained on the basis of their molecular structure.

INTRODUCTION

Historically, the dye industry has been linked with the development of synthetic organic chemistry. Although dyes have been extracted from natural sources for centuries, it was not until 1856 that a synthetic dye was produced commercially.[1,2] Azo compounds are the first compounds encountered that, as a class, are strongly coloured. They can be intensely yellow, orange, red, blue or even green depending upon the exact structure of the molecule. Because of their colour, the azo compounds are of tremendous importance as dyes; about half of the dyes in industrial use today are azo dyes which are mostly prepared from diazonium salts.[3]

The structural features that lead to colour are > C=C <, N=O, N=N, aromatic rings, C=O and NO_2. Most importantly, the azo (-N=N-) and nitroso (-N = O-) groups invariably confer colour and others do so under certain circumstances.

Dyes have been used to give multi-colour effects to anodized aluminium surfaces[4-9]. Also, cyanine dyes have been reported as efficient corrosion inhibitors on metal-corrodent systems[10-11] In this paper, the author seeks to obtain an insight into the effect of some azo dyes (viz. metanil yellow, naphthol blue black and solochrome dark blue) on the corrosion of mild steel in hydrochloric acid using the weight loss technique. The effect of molecular structure on the corrosion inhibition has been incorporated into this study.

EXPERIMENTAL

Materials

The mild steel sheets used for this study have the same composition as reported earlier[11-12]. The mild steel sheets were mechanically press-cut into coupons of dimension 3cmx4cmx0.07cm. The two faces had 24.0cm^2 total geometric surface area. Holes were drilled at one end of the coupons. These coupons were used as supplied without further polishing. However, surface treatment of the coupons involved degreasing in absolute ethanol and drying in acetone (NACE). The treated coupons were then stored in a desiccator before their use in corrosion studies.

The inhibitors used for the present study are azo dyes namely metanil yellow, naphthol blue black and solochrome dark blue. These dyes were obtained from Aldrich Chemical Company Inc. USA and were used without further purification. The thermostated water bath used was a GFL:M Jurgen & Co. England model.

Studies on the corrosion effects of HC1 on the mild steel coupons were carried out by observing preweighed steel coupons in HC1 solutions having concentrations of 0.OM, 0. 1M, 0.2M, 0.3M, 0.4M

and 0.5M for 5 hours in a water bath thermostated at 30°C and 40°C.

In each test for corrosion inhibition, a set of test mixtures was prepared in six beakers each containing 0.5M HCl and one of $1x10^{-5}$M, $1x10^{-4}$M, $1x10^{-3}$M, $1x10^{-2}$ M, $1x10^{-1}$M and 0.0M of the respective inhibitor. These beakers were labelled A,B,C,D, E and F, the last being the experimental blank. These mixtures were prepared for metanil yellow, naphthol blue black and solochrome dark blue azo dyes.

Weight loss determination

In each of the corrodent/inhibitor test mixtures of each inhibitor dye, a mild steel coupon of known weight was suspended with the help of a glass hook and rod. The beakers containing the metal-corrodent/inhibitor systems were put into a thermostated water bath maintained at 30°C and 40°C and readings taken after 5 hours. At the end of 5 hours, each coupon was retrieved from its test solution, washed several times in 20% NaOH containing 200g/l of zinc dust until clean, dried in acetone and reweighed. The difference in weights was taken and the weight loss evaluated in mg/dm^2, each value being the average of three determinations under the same test conditions.

RESULTS AND DISCUSSION

Appearance of corroded coupons

The mild steel specimens immersed in dilute solutions of the acid were covered with a greyish loose, thin film which was removed easily by rubbing with a rubber bung. A similar observation was made by Talati and Daraji[13]. In concentrated acid, the film became thicker and dark grey in appearance. The inhibited acid specimens were covered with a loose film of the same colour as the dye used and was also easily removed by the cleaning solution described earlier.

Corrosion by HCl

The corrosive effect of HCl on mild steel increased with the acid concentration; it became vigorous at 0.5M HCl concentration. Hence, 0.5M HCl was selected for the observation of the inhibitive effect of the dyes under test.

Corrosion inhibition by test dyes

The effects of the test *inhibitors* are shown in figures 1 and 2. The corrosion rate is higher in the blank 0.5M HCl solution than it is in the solutions containing inhibitors. The corrosion inhibitive effect of each test dye increases as the dye concentration increases. Also the corrosion rate is higher at 40°C than at 30°C in all cases. The increase in corrosion rate with temperature is reasonable and is in agreement with a report[14] that a doubling in reaction rate is expected with a 10°C rise in temperature.

Figures 1 and 2 reveal the most effective inhibitor among those tested to be metanil yellow and the order of effectiveness of the inhibitors as Metanil yellow >Solochrome dark blue > Naphthol blue black.

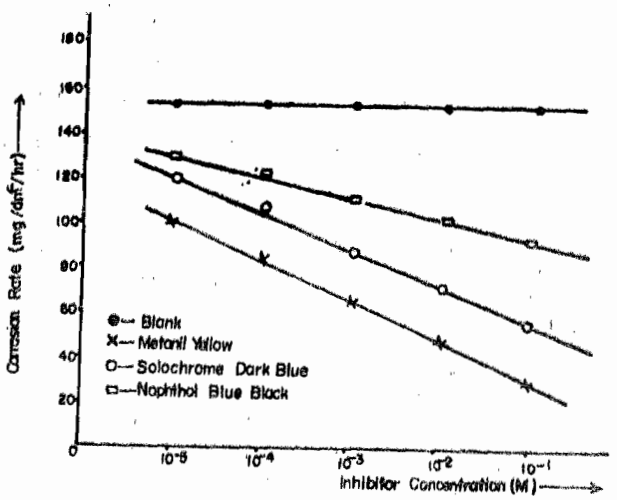


Fig. 1. Variation of corrosion rate ($mg/dm^2/hr$) with inhitor concentration for mild steel coupons in 0.5M HCl solution containing various inhibitors at 30°C.

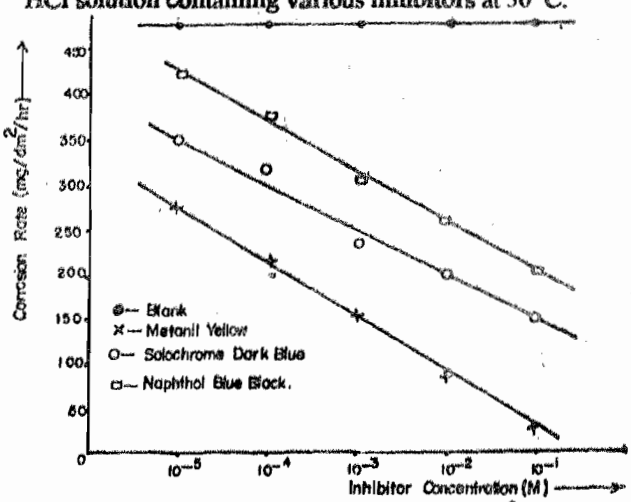


Fig. 2. Variation of corrosion rate ($mg/dm^2/hr$) with inhitor concentration for mild steel coupons in 0.5M HCl solution containing various inhibitors at 40°C.

Figures 3-4 reveal that the inhibitor efficiency increases with increase in inhibitor concentration.

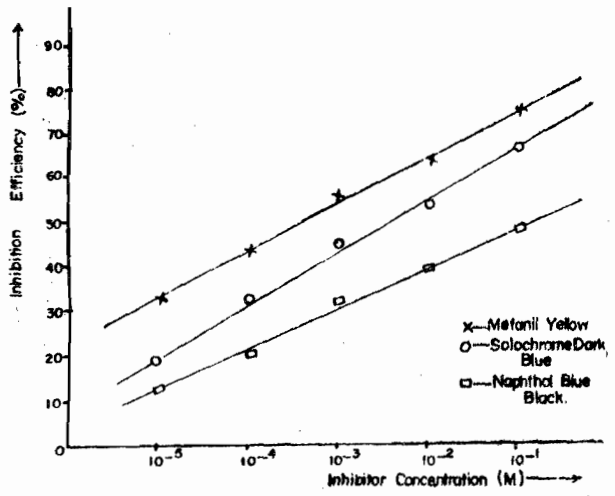


Fig. 3. Variation of inhibition efficiency (%) with inhitor concentration for mild steel coupons in 0.5M HCl solution containing various inhibitors at 30°C.

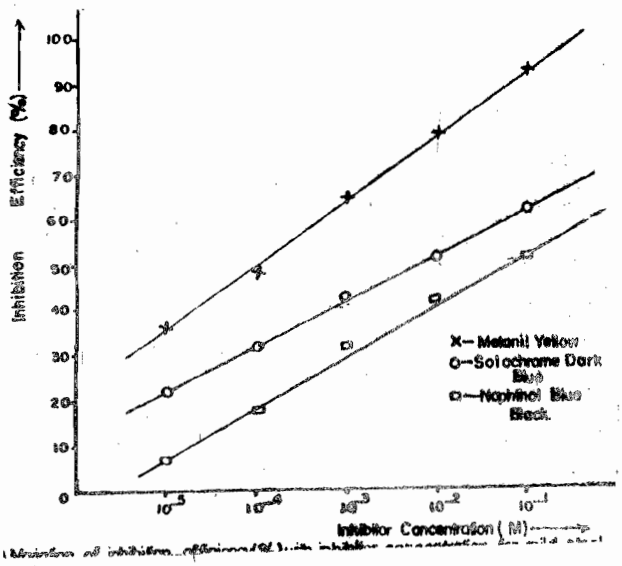


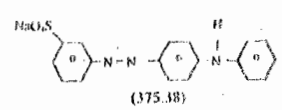
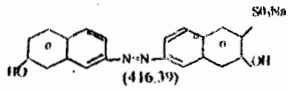
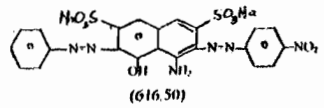
Fig. 4. Variation of inhibition efficiency (%) with inhitor concentration for mild steel coupons in 0.5M HCl solution containing various inhibitors at 40°C.

Comparison of corrosion inhibition behaviour

From Figures 3 and 4, it is observed that metanil yellow (18 carbon atoms; mol. wt 375.38) inhibits the acid corrosion of mild steel better than solochrome dark blue (20 carbon atoms; mol. wt. 416.39) and Naphthol blue black (22 carbon atoms; mol. wt 616.50). The highest inhibition efficiency of 93% is obtained for metanil yellow while 65% is obtained for solochrome dark blue and 53% for Naphthol blue black at 40°C and inhibitor concentration of 10^{-1}M. All the inhibitors are generally more effective at 40°C than 30°C. The variation of inhibition efficiency with temperature is a very important tool often times used to deduce the mode of adsorption of the inhibitors[13]. For a chemical adsorption mechanism, the inhibition efficiency increases with increase in temperature while an increase in inhibition efficiency with decrease in temperature is suggestive of a physical adsorption mechanism. The mechanism of chemical adsorption is therefore proposed for the present inhibitors and the activation energies, E calculated from the Arrhenius equation are Naphthol blue black (53.62 KJ/mol), Solochrome dark blue (73.77KJ/mol) and metanil yellow (82.85KJ/mol) which is in good agreement with reports by Talati and Modi[15] and Barrow[16] that the activation energy for chemical adsorption mechanism should be greater than 40KJ/mol (Table 1). Since chemical adsorption mechanism is proposed for the present inhibitors, a mono-layer protective coverage is expected on the entire mild steel surface by the inhibitors for the inhibition to be effective. The molecular structure of the azo dyes studied are shown in Table 1.

Figures 3-4 reveal that inhibition efficiency decreases with increase in molecular weight for the azo dyes studied eventhough all the dyes inhibit via chemical adsorption mechanism. This could be explained in terms of the possibility of disrupting the monolayer formed by higher molecular weight compounds. The bulkiness of the inhibitors is a disadvantage in chemisorption mechanism as this could lead to the development and propagation of cracks through the suppression of the monolayer. The development of such cracks is disastrous to the protection of the metal since the corrodent could penetrate the monolayer through these cracks and thereby come to contact with the metal surface leading to a reduction in inhibition efficiency. The results obtained in this study are also supported by

Table 1. Calculated values of activation energy (E_a) of the azo dyes at different concentrations in 0.5M HCl.

Inhibitor	Molecular Formula (molecular wt)	Inhibitor Conc (M)	Activation energy E_a KJ/mol.	Average, E_a (KJ/mol)
Metanil Yellow	 (375.38)	10^{-1}	72.58	
		10^{-2}	72.58	
		10^{-3}	99.24	82.85
		10^{-4}	87.02	
		10^{-5}	72.51	
Solochrome dark blue	 (416.39)	10^{-1}	72.58	
		10^{-2}	72.50	
		10^{-3}	77.69	73.77
		10^{-4}	77.69	
		10^{-5}	67.11	
Naphthol blue black	 (616.50)	10^{-1}	54.91	
		10^{-2}	54.91	
		10^{-3}	40.46	53.62
		10^{-4}	54.90	
		10^{-5}	64.23	

Talati and Joshi[14] who used Congo red, methyl red, methyl orange as inhibitors for aluminium in aliphatic amines, that congo red (696.9 mol.wt) has inhibitive efficiency less than methyl orange (327.24) and methyl red (291.29). Congo red is a large molecule with two azo bonds having 4-amino-l-naphthalenesulfonic acid groups at each end. The inhibitors used in this study can be classified structurally as follows:

(a) Dye containing three nitrogens, two from the azo group, one from the NH group and three benzene rings and one SO_3Na e.g. metanil yellow.

(b) Dye containing two nitrogen (from the azo group), two naphthalene rings, one SO_3Na group and two OH groups e.g. Solochrome dark blue and

(c) Dye containing six nitrogens, four from two azo groups, one from NH_2 group and one from NO_2 group, one naphthalene ring, two SO_3Na groups and one OH group e.g. Naphthol blue black.

This classification would explain that Naphthol blue black which contains two azo groups, two SO_3Na groups in ortho position to the two azoic nitrogens, an -OH group in ortho position to the azoic nitrogen and an NH_2 group in ortho position to the azoic nitrogen as compared to metanil yellow and solochrome dark blue has less inhibitive efficiency because of the bulkiness of the group in its structure.

CONCLUSION

The inhibition efficiency of the inhibitors studied increases with increase in temperature and decreases as molecular weight increases. Metanil yellow exhibits a better inhibition efficiency of 93 % than solochrome dark blue *(65%)* and Naphthol blue black *(53%)* at 40°C. The mechanism of chemical adsorption is proposed on the basis of the calculated values of the activation energy.

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