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INHIBITION OF IRON BY WATER SOLUBLE POLYANILINE IN ACID CHLORIDE MEDIUM

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The corrosion inhibition of iron in acid chloride solution offered by a new class of water soluble, commercially available acid black II, has been studied. Corrosion inhibition property was evaluated by the Tafel extrapolation method, electrochemical impedance spectroscopy and weight loss methods. The results indicate that the acid black II is capable of inhibiting the corrosion of iron in 1 *M* HCl by 95% at 100 ppm level.

Keywords: Polyaniline, corrosion inhibitor, impedance spectroscopy

INTRODUCTION

Corrosion of iron and its control is an active area of research due to its high industrial importance. The control of this corrosion assumes greater significance, particularly by the use of inhibitors due to its easy methodology. The acid inhibitors find extensive applications as component in pretreatment, acidizing of oil wells, cleaning of boilers and heat exchangers etc.

Literature shows that the extensively used acid inhibitors are organic compounds having unsaturated bonds [1-3]. This unsaturated and other functional groups such as -NH, -N=N-, -CHO, R-OH and R=R in organic compounds imparts extraordinary property of adsorption over active metal surface by replacing the water molecule at the interface to protect the metal from corrosion. This reaction can be represented as

$$Org_{(sol)} + nH_2O \longrightarrow Org_{(s)} + nH_2O_{(sol)}$$

Hence, the inhibition efficiency of an inhibitor depends on the extent of the adsorption of inhibitor and its coverage over the metal surface. In addition to the functional groups present in the inhibitor, its molecular dimension, orientation and their solvation property [4,5] also influence the adsorption characteristic thereby to influence its inhibition efficiencies.

Recently, we have reported [6,7] the use of methoxy and ethoxy aniline and its polymers as effective corrosion inhibitors having very high inhibition efficiencies at low ppm levels, while their monomer offered only 50% at 20,000 ppm indicating how the molecular size and delocalisation are responsible for better adsorption over the metal surface and hence the corrosion inhibition.

In this paper, our recent results concerning the inhibitive action of acid black II on the corrosion of iron in acidic chloride medium are presented. Though poly-ethoxy aniline (PEA) and poly-methoxy aniline (PMA) may offer very good inhibition efficiencies, their solubility in water is poor and hence may not be of much practical application. The results discussed in this paper on acid black II though offer little less inhibition efficiencies compared to PEA and PMA, its complete water solubility is of high practical importance. Acid black II is widely used for the negative staining of bacteria and is used with basic fuchsin for staining bacterial spores. The inhibition properties has been evaluated by the Tafel extrapolation method (TEM), electrochemical impedance spectroscopy (EIS) and weight loss methods (WL).

EXPERIMENTAL

Acid black II, the water soluble derivative of aniline and nitrobenzene, was procured commercial (Aldrich) and used without further purification. The electrochemical experiments TEM and EIS were carried out using three electrode system with 1 cm^2 pure ion (99.98% purity) as working electrode, platinum foil as counter electrode and saturated calomel

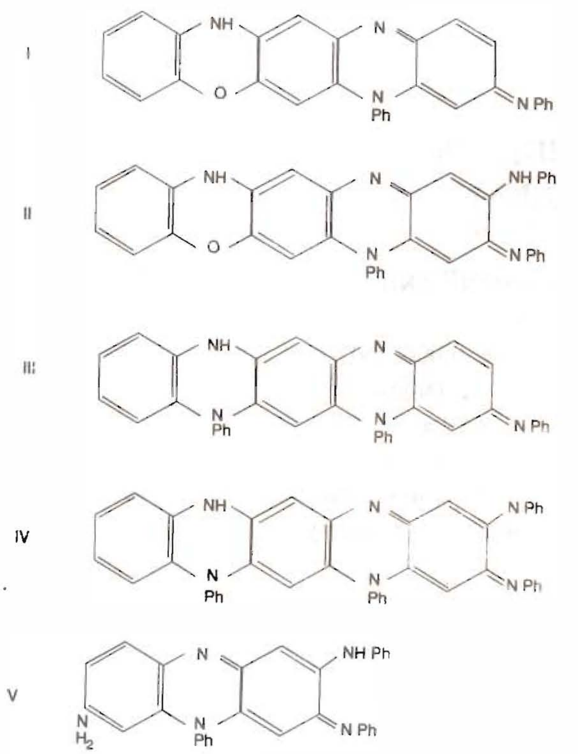

Fig. 1: Possible resonant structures of acid black II

electrode (SCE) as reference electrode. Solutions were prepared using AR grade chemicals with triple distilled water.

An EG & G potentiostat (Model 173) with universal programmer (Model 175) along with X-Y recorder (Hewlett Packard Model 7500) has been used for Tafel extrapolation method. An electrochemical system (with EG & G PAR digital potentiostat model 273, lock-in analyzer model 5208 and an IBM PC) was used for impedance measurements. For weight loss experiments three samples of area 10 cm^2 have been exposed to the test solution for 2 hours and the average weight loss was determined.

TABLE I: Corrosion inhibition efficiencies evaluated by weight loss method

Medium	Weight loss $mg.h^{-1}$	IE %
1 N HCl (Blank)	6.100	-----
+ 10 ppm	1.861	69.5
+ 25 ppm	1.220	80.0
+ 50 ppm	0.679	88.9
+ 100 ppm	0.584	90.4

RESULTS AND DISCUSSION

The acid black II structure is shown in Fig. 1. The average weight loss on exposing three pure iron samples of area 10 cm^2 each to the test solution for 2 hours has been recorded in Table I. The inhibition efficiency is estimated by

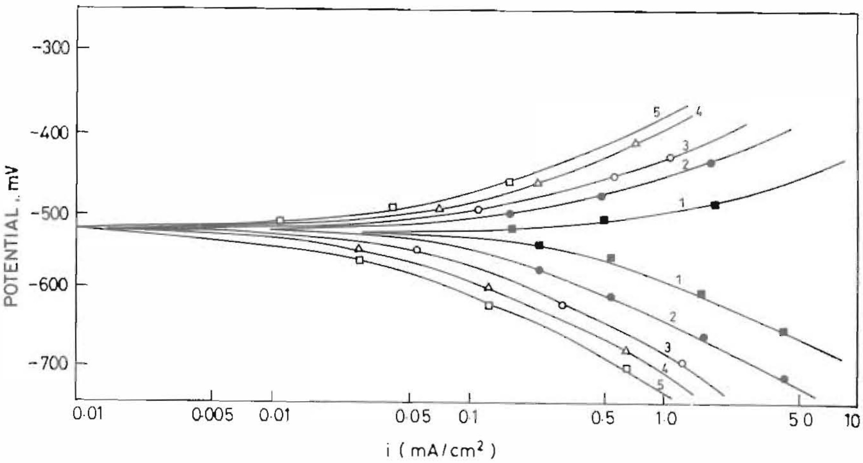

Fig. 2: Polarisation behaviour of iron in 1 N HCl with the addition of acid black II
(1) 1 N HCl (■) (2) 1 N HCl + 10 ppm AB II (●) (3) 1 N HCl + 25 ppm AB II (○)
(4) 1 N HCl + 50 ppm AB II (△) (5) 1 N HCl + 100 ppm AB II (□)

TABLE II: Corrosion inhibition efficiencies evaluated by Tafel extrapolation method

Medium	E_{corr} mV_{SCE}	I_{corr} $\mu A/cm^2$	b_a mV/dec	b_c mV/dec	IE %
1 N HCl (blank)	-515	340	45.0	110	-----
+ 10 ppm	-510	86	48.0	108	74.7
+ 25 ppm	-508	42	50.0	112	87.6
+50 ppm	-496	21	52.0	112	93.8
+ 100 ppm	-488	13	54.5	115	96.2

$$IE\% = \left(\frac{1 - WL_i}{WL}\right) \times 100$$

where WL and WL_i are the weight losses without and with the addition of inhibitors.

A typical potentiodynamic polarisation curve showing the inhibitive action of acid black II is given in Fig. 2. The corrosion parameters obtained from these curves are presented in Table II.

The increase in both anodic and cathodic polarisation with the addition of inhibitor indicates its mixed type control. Also, as expected, with the increase in inhibitor concentration the inhibition efficiency also increased. The anodic Tafel slope also increases with inhibitor addition. In the case of dissolution of iron, it is generally considered [8], a stable adsorbed (FeOH) intermediate is formed. The presence of organic molecules (In) probably leads to the formation of a stable chelates [(FeOH).In] on the iron surface. The presence of this surface complex reduces the rate of anodic dissolution of iron by changing the reaction mechanism [9] as indicated by the increase in b_a.

The inhibition efficiencies were calculated by

$$IE\% = \left(\frac{I - I_{corri}}{I_{corr}}\right) \times 100$$

where I_{corr} and I_{corri} are the corrosion current density in the absence and presence of inhibitor. It is seen from the Table II that the acid black II is able to inhibit 85% even at 25 ppm.

The electrochemical impedance spectroscopy is one among the most successful techniques used to evaluate the usefulness of an inhibitor. The Nyquist plot of the complex impedance of iron in 1 **N** HCl with and without the addition of acid black II is given in Fig. 3. As can be seen from figure, the Nyquist plots are depressed semicircles with centres below the real axis.

The cause for this depression and the method of extracting kinetic parameters have been discussed in detail [7].

In this study, the corrosion parameters were obtained using nonlinear least square fit using a computer and are presented in Table III. The series resistance, the high frequency response, is almost zero and is unaffected by the addition of inhibitor whereas the charge transfer resistance, the low frequency response, increases with inhibitor concentration.

The inhibition efficiency is calculated using the relationship

$$IE\% = \left(\frac{1 - R_{ct}}{R_{cti}}\right) \times 100$$

where R_{ct} and R_{cti} are the charge transfer resistances without and with the addition of inhibitors. The surface coverage over the iron surface, which is calculated from the double layer

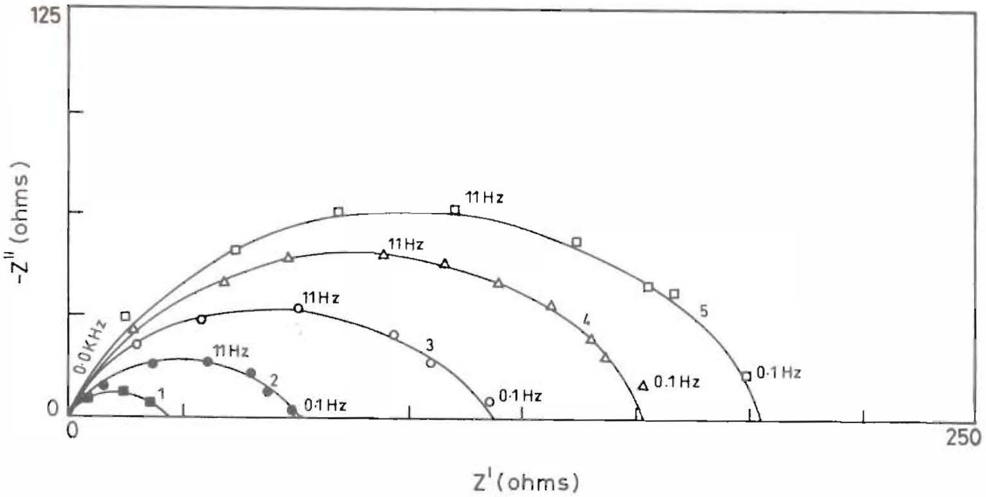

Fig. 3: Nyquist plots for iron in 1 N HCl with the additionof acid black II
(1) 1 N HCl (■) (2) 1 N HCl + 10 ppm (●) (3) 1 N HCl + 25 ppm (○) (4) 1 N HCl + 50 ppm (△) (5) 1 N HCl + 100 ppm (□)

TABLE III: Corrosion inhibition efficiencies evaluated by electrochemical impedance spectroscopy

Medium	R_p Ω cm^2	IE %	C_{dl} μF . cm^{-2}	Surface coverage θ
1 N HCl				
(Blank)	22.6	-----	910.8	-----
+ 10 ppm	71.2	68.3	415.0	0.54
+ 25 ppm	123.6	81.7	267.7	0.71
+ 50 ppm	171.4	86.8	203.9	0.78
+ 100 ppm	206.0	89.0	119.8	0.87

capacitance, shows an increase with increase in the inhibitor concentration. The inhibition efficiencies obtained by these electrochemical methods are in good agreement with those obtained from the weight loss method, which is a non-electrochemical method.

As given in the structures, the three nitrogens are in cycling ring structure and two nitrogens, = N-Ph and NHPh are outside the ring. The outside nitrogens are capable of forming a quarternary ammonium salt. Thus this large cations gets adsorbed on the metal surface offer a high degree of corrosion inhibition.

CONCLUSION

This study suggests that commercially available, water soluble, acid black II which has a structural similarity to polyaniline but is less rigid in the structure due to the absence of change carriers can prove to be a very good corrosion inhibitor for iron under acidic condition. Results showed inhibition efficiency upto 95% can be obtained with 50 ppm of acid black II.

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