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CORROSION INHIBITION OF Al-PURE BY ANILINE-N-BENZYLIDENE (ANB) A SCHIFF BASE AS INHIBITOR IN HYDROCHLORIC ACID.

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ABSTRACT

The corrosion behavior and mechanism of ANB with different concentrations in hydrochloric acid was studied by chemical method (weight loss) and electrochemical technique (galvanostatic polarization). The inhibition efficiency of ANB increased as the concentration of ANB increased. At the optimum concentration of 0.001% of ANB, it gives inhibition of 56.4% and 0.5% concentration gives 99.0% inhibition and maximum inhibition, i.e.; 99.9% is achieved at 1.0% concentration. The inhibitor is found to be an excellent corrosion inhibitor from the results obtained. The adsorption of this compound on the metal surface is found to obey Langmuir isotherm. The inhibition action depends on the chemical structure, concentration of the inhibitor and the concentration of the corrosive medium. Galvanostatic polarization data indicates that this inhibitor is of mixed type with predominant effect on cathode. The better efficiency of ANB is due to presence of an iminic group ($>C=N-$). Results obtained from the chemical method and electrochemical technique is in good agreement with each other.

Key words: Corrosion, Al-Pure, ANB, Weight loss, Galvanostatic polarization.

INTRODUCTION

Aluminium and its alloys are widely used in many industries such as reaction vessels, pipes, machineries, chemical batteries, automobiles, food handling, building, electrical transmission, etc [1] because of its low cost, light weight, high thermal and electrical conductivity [2]. When aluminium exposed to air, a layer of aluminium oxide forms almost instantaneously on the surface of aluminium. This layer has excellent resistance to corrosion. It is fairly resistant to most acid and alkali solution because of its amphoteric nature.

Solutions of hydrochloric acid, when used for pickling of aluminium or in chemical and electrochemical etching of aluminium lithographic plates or condenser films [3], dissolve the metal to a considerable extent. It is, therefore, desirable to inhibit the solution used for pickling which can be done by the use of inhibitors, which is one of the best known methods for the protection of corrosion [1]. Inhibitors for the corrosion of metals are chemical compounds, when present in small quantities in an aggressive medium, inhibit corrosion by bringing about changes in the surface condition of a metal. This process can be associated either with adsorption of the inhibitor or the formation of difficulty-soluble films which, however, are significantly thinner than protective coatings [4].

From the literature survey [5 - 7], it is observed that among all the inhibitors studied so far Schiff bases are found to be very effective. Schiff base as an inhibitor is synthesized from relatively two basic materials (amine and aldehyde) and the inhibition depends upon formation of a chemically adsorbed film and forming a complex with the metal surface. The ability of the inhibitor is to form a long lasting film and it depends upon its chemical structure and interaction with the corrosive environment [8].

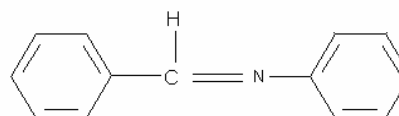
In the present work, Aniline-N-benzylidene (ANB) has been reported as corrosion inhibitor for Al-Pure in hydrochloric acid. Both weight loss and galvanostatic polarization methods were used in the evaluation of ANB.

MATERIALS AND METHODS

Synthesis of Schiff base

The Schiff base was synthesized by condensation of benzaldehyde with aniline in the presence of ethyl alcohol as per the procedure described by Jaeger [9].

ANB (light yellow crystalline product, m.p., 52°C, registry number, 538-51-2) is insoluble in water but soluble in ethanol. The structure of the inhibitor is shown below:



Aniline-N-benzylidene (ANB)

Preparation of specimens

Rectangular specimens of Al-Pure, of size 6 cm × 3 cm (thickness 0.050 cm), with a small hole of ~2 mm diameter just near one end of the specimen were used for the determination of the corrosion rate. The specimens were polished using successively “0” to “0000” Oakey emery paper. The final polishing was done using jewelers rough, which gave a mirror-like finish. The specimens were finally degreased by A.R. carbon tetrachloride (sulphur free). The test specimens were exposed to 1.0 M and 2.0 M hydrochloric acid solutions, containing addition of ANB in the range 0–1.0%. One specimen only was suspended by a Pyrex glass hook in each beaker containing 230 ml of the test solution which was open to the air at 35° ± 0.5°C (unless otherwise specified) to the same depth of about 1.3 cm below the surface of the liquid.

Polarization measurements

For polarization studies, metal coupons of circular design, diameter 2.802 cm with a handle 3 cm long and 0.5 cm wide were used. The handle and the back of the coupon and of the auxiliary platinum electrode were coated with Perspex leaving only the circular portion of the specimen exposed of apparent surface area, 6.156 cm². The solution, 80 ml in each limb, was contained in an H-type Pyrex glass cell with the Luggin capillary as near to the electrode surface as possible and a

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porous partition to separate the two compartments. The potential was measured against a saturated calomel reference electrode (SCE). Galvanostatic polarization data were obtained with Wenking Potentiostat POS 73. In these experiments, the current density was varied in the range of 2×10^{-4} to 3.25×10^{-4} A cm⁻².

RESULTS AND DISCUSSION

Effect of inhibitor concentration

To study the effect of inhibitor concentration on inhibitive efficiency of the inhibitor, weight losses were determined in 1.0 M and 2.0 M hydrochloric acid containing various concentrations of inhibitor at $35 \pm 0.5^\circ\text{C}$ for exposure periods of 60 minutes and 15 minutes respectively. The inhibitor efficiency (%) was calculated as follows:

$$\text{Inhibitor efficiency (\%)} = \frac{W_u - W_i}{W_u} \times 100 \quad [1]$$

where W_u = weight loss in uninhibited acid, and W_i = weight loss in inhibited acid.

The results given in Table-1, show that a specimen of Al-Pure when immersed in plain acid suffers a weight loss of 2300 mgdm⁻² in 1.0 M HCl for an exposure period of 60 minutes and 4236 mgdm⁻² in 2.0 M HCl for an exposure period of 15 minutes, with evolution of hydrogen.

Table - 1 Effect of inhibitor concentration on weight loss and inhibitor efficiency for Al-Pure in 1.0 M and 2.0 M hydrochloric acid. (Temperature : $35 \pm 0.5^\circ\text{C}$)

Inhibitor concentration % (W/V)	1.0 M HCl Exposure period : 60 min.		2.0 M HCl Exposure period : 15 min.	
	Weight loss (mg/dm ²)	Inhibitor efficiency (%)	Weight loss (mg/dm ²)	Inhibitor efficiency (%)
Nil (HCl only)	2300	-	4236	-
<i>Aniline-N-benzylidene(ANB)</i>				
0.001	1003	56.4	732	82.7
0.005	894	61.1	596	85.9
0.05	461	80.0	230	94.6
0.10	260	88.7	138	96.7
0.50	22	99.0	16	99.6
0.80	8	99.7	11	99.7
1.00	3	99.9	5	99.9

Addition of small quantities (viz., 0.001%) of inhibitor to 1.0 M HCl show low inhibition (56.4%) toward the corrosion of Al-Pure in the use of ANB. As the concentration of the inhibitor is increased, the weight loss due to corrosion decreased and almost (99 – 100%) protection could be achieved with 0.5 – 1.0% of the inhibitor concentration.

Here also, in 2.0 M HCl, as the concentration of the Schiff base is increased, it confers more protection and at 0.05% inhibitor concentration the inhibition is found to be 94.6% and at 0.5% concentration, it confers 99.6% protection. This shows that the inhibitor is effective in higher concentration of the acid. From the results, it appears that the presence of iminic group (>C=N-) in the molecule plays a significant role in conferring the good inhibition. When plot of $\log (\theta / (1-\theta))$ vs $\log C_{inh}$ (inhibitor concentration) was drawn (Figure-1), straight line was obtained indicating that the ANB was adsorbed onto the metal surface following Langmuir isotherm [10].

$$C_{inh} = \theta / K (1-\theta) \quad [2]$$

where, θ is the fraction of the area covered by the inhibitor.

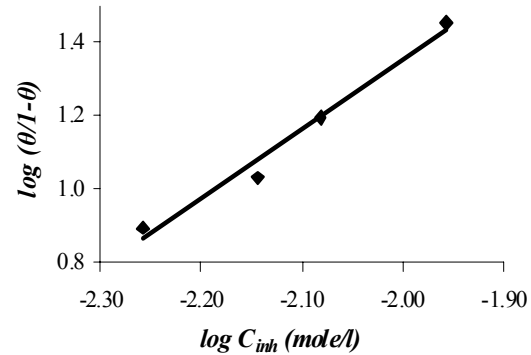


Fig. 1 Langmuir plot for ANB in 1.0 M hydrochloric acid at 35°C .

Galvanostatic polarization measurement

The effect of current density on the cathode and anode potentials of Al-Pure in 1.0 M HCl, plain as well as inhibited is shown in Figure-2. A specimen of Al-Pure immersed in 1.0 M HCl develops of corrosion potential of -843 mV (SCE). In acid containing effective concentration of the inhibitor the weight loss due to corrosion is decreased considerably but the corrosion potential remains almost constant. This shows that the inhibitor is adsorbed quite generally on the metal surface and covers both, the anodic as well as the cathodic regions. It is also observed that with lower inhibitor concentration the potentials are less negative but as the inhibitor concentration is increased the potentials become more negative. This suggests that first the inhibitor is adsorbed on the anodic sites and as its concentration increases the cathodic sites are also covered. Galvanostatic polarization curves show negligible anodic but significant cathodic polarization in plain as well as inhibited acid.

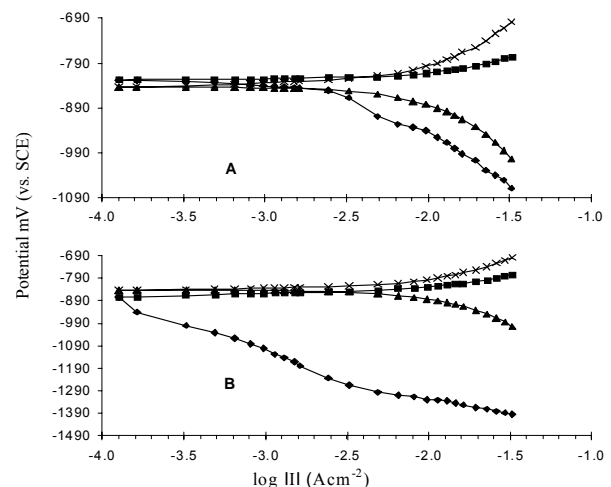


Fig. 2 Effect of current density on the cathode and anode potentials of Al-Pure in 1.0 M hydrochloric acid alone and in the presence of ANB.

- A ▲...▲ Cathodic potential in 1.0 M hydrochloric acid alone
 x.....x Anodic potential in 1.0 M hydrochloric acid alone
 ◆.....◆ Cathodic potential with 0.001% ANB
 ■.....■ Anodic potential with 0.001% ANB
 B ▲...▲ Cathodic potential in 1.0 M hydrochloric acid alone
 x.....x Anodic potential in 1.0 M hydrochloric acid alone
 ◆.....◆ Cathodic potential with 0.5% ANB
 ■.....■ Anodic potential with 0.5% ANB

Table – 2 Tafel parameters

Inhibitor and its concentration (%)	Tafel slope b		Corrosion current, i_{corr} , from		Inhibitor efficiency (%) from		
	Anodic V/decade	Cathodic V/decade	Extrapolation of cathodic Tafel line at E_{Corr}	Extrapolation of anodic Tafel line at E_{Corr}	From (4)	From (5)	Weight loss data (60 min)
1	2	3	4	5	6	7	8
1 M HCl Blank	0.113	0.120	4.467×10^{-3}	3.311×10^{-3}	-	-	-
ANB 0.001%	0.033	0.150	1.621×10^{-3}	1.737×10^{-3}	61.1	20.6	56.4
ANB 0.5%	0.076	0.118	1.621×10^{-6}	2.229×10^{-3}	>99.9	32.7	99.0

The Tafel parameters and inhibitor efficiencies calculated from the polarization data are given in Table-2. The inhibition efficiencies obtained by extrapolation of the cathodic Tafel line to corrosion potential agree well with those calculated from weight loss data. This suggests that in presence of ANB, both cathode and anode are polarized to a greater extent. ANB thus appears to be mixed type inhibitor with predominant action on the cathode.

Mechanism of inhibition

In general, most of the organic corrosion inhibitors are compounds with at least one polar unit having atoms of nitrogen, sulphur, oxygen and in some cases selenium and phosphorous. The polar unit is regarded as the reaction centre for the establishment of the adsorption process. In such a case the adsorption bond strength is determined by the electron density on the atom acting as the reaction centre and by the polarisability of the functional unit. Thus polar organic compounds acting as corrosion inhibitors are chemically adsorbed on the surface of the bulk metal, M, forming a charge transfer complex between the polar atom/ atoms and the metal: $M + R_nX \leftrightarrow M : XR_n$ [3]

According to Aramaki *et al.* [11], the metal and the compound are Lewis acid and base respectively and hence the stability of the adsorption bond is closely related to the hard and soft acids and bases principle. The bulk metal is classified as the soft acid and a molecule or ion of the soft base is readily chemisorbed on the metal surface by forming a stable donor-acceptor bond. Those inhibitors which are in a distinct ionic form may also get attached to the metal surface of opposite polarity through electrostatic attraction. The adsorbed monolayer will then block the dissolution of the metal. The size, shape and orientation of the molecule, and the electronic charge on it, will determine the degree of adsorption and hence the effectiveness of the inhibitor.

ANB contains seven conjugated double bonds (three in each of the aromatic ring and one in the iminic group) and have three anchoring sites (one iminic $>C=N-$, and two aromatic rings). The plot of $\log \theta / 1-\theta$ vs $\log C_{\text{inh}}$ shows that ANB function through adsorption following Langmuir adsorption isotherm. It appears that there are three anchoring sites through which the molecule can get adsorbed on the metal surface: the iminic group ($>C=N-$) and the delocalized π -electrons of the two aromatic rings. If it is assumed that when a compound form onium ion in acidic media and move to the cathodic region than the adsorption will take place through the iminic nitrogen and the delocalized π -electrons of the benzene moiety [12, 13], then a compound show good protection.

ANB confers good protection to Al-Pure in hydrochloric acid when present in sufficient amount and function through adsorption on the metal surface. Galvanostatic polarization data have shown that the action of ANB is of mixed type inhibitor with predominant effect on cathodic region.

CONCLUSION

1. ANB confers more than 99% protection to Al-Pure in hydrochloric acid at 0.5% inhibitor concentration.
2. The adsorption follows Langmuir isotherm.
3. Galvanostatic polarization measurement shows that the inhibitor is of mixed type with predominant effect on the cathodic region.
4. The presence of seven conjugated double bonds including an iminic group appeared to be the main factor enhancing chemisorption of an inhibitor.

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