



CORROSION INHIBITION OF ALUMINIUM IN HCl ACID SOLUTION BY ORTHO SUBSTITUTED SALICYLIDENE

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ABSTRACT

Mass loss has been used to study the inhibition of aluminium corrosion in HCl solution by ortho substituted aniline-N-salicylidene. The value of inhibition efficiency obtained by the mass loss method is in good agreement and depends upon the inhibitor, the acid, period of exposure and temperature. The thermodynamic parameters for adsorption of o-substituted aniline-N-salicylidenes for the corrosion of aluminium in 1N HCl were calculated.

Key words: Corrosion inhibitor, Aluminium, Acid, Ortho substituted Salicylidene.

INTRODUCTION

Aluminium is the most widely used non-ferrous metal in all the fields of industrial and domestic applications such as transportation, packaging, construction, a wide range of household items, Outer shell of consumer electronics and electrical transmission etc. Aluminium is remarkable for the low density and for its ability to resist corrosion due to the phenomenon of Passivation¹⁻³. When exposed, acid or alkaline condition destroy the the protective coating and corrosion of aluminium occurs, yielding Al^{+3} ion in acid and AlO_2 in the alkaline medium⁴. Acid pickling is widely used for aluminium surface treatment. Aluminium can be reacted with hydrochloric acid to produce hydrogen gas. Chloride ions of the HCl cause a substantial loss of the metal by corrosion and Cl^- ions of the acid create extensive localized attack⁵. Hence to avoid attack on the base metal during pickling and cleaning aluminium surfaces with acidic solutions, the use of inhibitors become necessary.

Acid inhibitors have been widely applied in the industrial field in pretreatment composition and as cleaning solution for plant equipments. Various organic compounds are reported as good corrosion inhibitors for aluminium in hydrochloric acid media⁶⁻¹⁴. The inhibiting effect of some Schiff bases on the corrosion of aluminium in HCl has been

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studied¹⁵⁻¹⁷. It has been observed that the corrosion inhibitors having nitrogen donor atoms exhibit wide range of corrosion inhibition activity towards aluminium.

The aim of the present investigation is to evaluate the efficiencies of Schiff bases derived from some ortho-substituted anilines and salicylaldehyde as corrosion inhibitors for aluminium in 1 N HCl solution. The effects of inhibitor concentration, exposure period, and temperature on the behavior of these inhibitors have been investigated using corrosion weight loss method.

EXPERIMENTAL

Specimen preparation

Rectangular specimen of aluminium of size 30 x 30 x 0.28 mm with a small hole of about 2 mm diameter near the upper edge of the specimen were used for the determination of corrosion rate. The specimen was polished using emery paper. The final polishing was done with a linen buffing wheel, which gave a mirror look-finish, then degreased by carbontetrachloride. Each specimen was suspended by a glass hook and immersed in a beaker containing 230 mL of the test solution at 297 ± 0.5 K and left exposed to air. Evaporation losses were made up with distilled water. The test specimens were cleaned with saturated ammonium acetate solution^{18,19}. Duplicate experiments were performed in each case and mean values of the mass were calculated.

Test solution preparation

The solution of 1 N HCl was prepared using doubly distilled water. The Schiff bases were synthesized by condensation of aniline, o-toluidine and o-aminophenol with salicylaldehyde in the presence of ethanol. The crude solids of the Schiff bases obtained were first washed with distilled water, then with very dilute hydrochloric acid and finally with water. Then the crude was purified by repeated recrystallization from ethanol. The test solution was 1 N HCl acid containing concentration of 0.1% to 0.4% of w/v Schiff bases, viz aniline-N-salicylidene (ANS), o-toluidine-N-Salicylidene (o-TNS) and o-aminophenol-N-salicylidene (o-HNS) contents. The acid solution was prepared by using AR grade reagent and inhibition solution.

Inhibition efficiency

The effectiveness of an inhibitor is addressed in terms of its inhibition efficiency (IE) given by –

$$IE (\%) = W_u - W_i / W_u \times 100$$

Where W_u and W_i are the weight loss of the metal in uninhibited acid and inhibited solution, respectively.

The weight losses are found by keeping exactly identical specimens for a fixed time and at constant temperature in the solution with and without inhibitors.

RESULTS AND DISCUSSION

Results of inhibitor concentration

Effect of inhibition efficiency (I.E.) was calculated from the mass loss measurement for 1 N HCl. It was found that efficiency of the various inhibitors increases in the following order at 0.1% concentration.

o-TNS (54.99%) < ANS (94.8%) < o-HNS (95.49%). At 0.3% concentration the inhibitor efficiency is found range from 24.96% (o-HNS) to 93.0% (ANS) whereas at 0.4% concentration o-HNS (38.81%) < ANS (98.7%) < o-TNS (99.36%) (Table 1).

Table 1: Inhibition efficiencies for aluminium in 1 N HCl with Schiff bases (Temp.: 297 ± 0.5 K, (Immersion time: 30 mins)

Inhibitor & its concentration	Weight loss in mg/dm^2 (% of Inhibitor efficiency η)			
Uninhibited	1711 (-)			
%	0.1	0.2	0.3	0.4
ANS	89 (94.80)	170 (90.06)	136 (93.0)	22 (98.70)
o-TNS	770 (54.99)	866 (49.39)	625 (63.47)	11 (99.36)
o-HNS	77 (95.49)	1292 (24.14)	1284 (24.96)	1047 (38.81)

Effect of immersion period

The effect of inhibition efficiency (I.E.) was calculated from the mass loss measurement for 1 N HCl. The effect of exposure period on inhibitor efficiency of different inhibitor at 297 K and 0.1% concentration (0.4% in the case of o-TNS) was studied. It was found that ANS and o-HNS inhibitors efficiency increased up to 90 min for 0.1% inhibitor

concentration but in case of o-TNS, inhibitor efficiency decreases up to 90 min for 0.4% inhibitor concentration (Table 2).

Table 2: Effect of exposure period on inhibition efficiencies for aluminium in 1 N HCl with Schiff bases (Temp. 297 ± 0.5 K)

Inhibitor & its concentration	Weight loss in mg/dm^2 (% of Inhibitor efficiency η)			
	Exposure period	30 min	60 min	90 min
Uninhibited acid soln		1711	2594	2414
ANS (0.1%)		89 (94.80)	27 (98.96)	125 (94.82)
o-TNS (0.4%)		11 (99.36)	254 (90.55)	117 (95.15)
o-HNS (0.1%)		77 (95.49)	232 (91.06)	37 (98.47)

Effect of temperature

To determine the effect of temperature on inhibitive efficiency, the weight losses were determined in 1 N hydrochloric acid containing 0.1% inhibitor (0.4% in case of o-TNS) at solution temperatures of 297, 307, 317 and 327 K. (Table 3).

Table 3: Effect of temperature on inhibition efficiencies for aluminium in 1 N HCl with Schiff bases for 30 min

Inhibitor & its concentration	Weight loss in mg/dm^2 (% of Inhibitor efficiency η)				
	Temperature (K)	297	307	317	327
Uninhibited acid soln		1711	2568	3730	4267
ANS (0.1%)		89 (94.80)	31 (98.79)	973 (73.91)	3118 (26.93)
o-TNS (0.4%)		11 (99.36)	17 (99.34)	15 (99.59)	53 (98.76)
o-HNS (0.1%)		77 (95.49)	33 (98.71)	2831 (24.10)	2083 (51.14)

It is seen that the extent of corrosion in inhibited as well as uninhibited acid increases with a rise in temperature, the loss in weight being much higher in plain acid. The results also show that the o-TNS decrease the corrosion rate to an appreciable extent, the extent of inhibition ranging from 98.76% to 99.59%. From the weight losses it may be generalized that here also o-TNS appears to be the best inhibitor.

The values of energy of activation, E_a , were calculated with the help of the equation -

$$\log \rho_2/\rho_1 = E_a/2.303 R \{1/T_1 - 1/T_2\} \quad \dots(1)$$

and also from the plots of $\log \rho$ vs $1/T$ where ρ is the corrosion rate at temperature T (K) and R is the gas constant (Fig. 2).

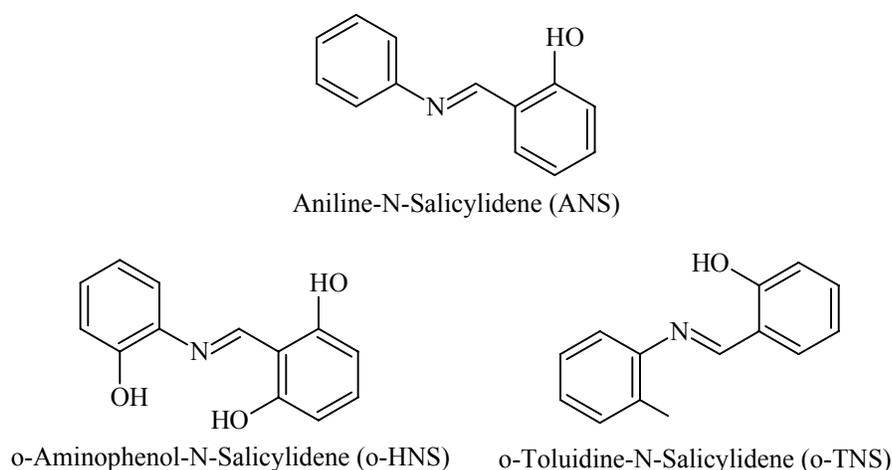


Fig. 1: Structural formula of ANS, o-HNS and o-TNS

From the E_a values, it is apparent that for the corrosion of aluminium in uninhibited acid the E_a value is 25 KJmol^{-1} whereas in inhibited acid the values are higher and range from 43 KJmol^{-1} (o-TNS) to 97 KJmol^{-1} (o-HNS). In inhibited acid, the E_a values thus vary and depend on the inhibitive power of the inhibitor. The higher values of activation energy in inhibited acid suggest that the adsorption of the inhibitor on the metal surface may be physical or weak in nature²⁰.

If it is assumed that the inhibitor is adsorbed on the metal surface in the form of a mono layer film, covering at any instant a fraction, θ , of the metal surface in a uniform random manner, then the heat of adsorption, Q_A of the inhibitor can be calculated from the equation:

$$Q_A = 2.303 R \left[\frac{\log \theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right] \left[\frac{T_1 T_2}{T_2 - T_1} \right] \quad \dots(2)$$

Where θ_1 and θ_2 are the fractions of the total surface covered by the inhibitors at temperatures T_1 and T_2 (k), respectively with –

$$\theta = \frac{(W_u) - (W_i)}{(W_u)} \quad \dots(3)$$

The values of free energy of adsorption (G_A^o) were calculated with the help of the following equation²¹ -

$$\log C_{inh} = \log \frac{\theta}{1-\theta} - \log B \quad \dots(4)$$

Where

$$\log B = -1.74 - \left(\frac{G_A^o}{2.30.RT} \right) \quad \dots(5)$$

From the values of Q_A and G_A^o , the values of the entropy of adsorption, S_A^o were also calculated. The values of these thermodynamic functions are given in Table 4.

Table 4: The thermodynamic parameters for adsorption of o-substituted aniline-N-salicylidenes for the corrosion of aluminium in 1 N HCl for 30 min

Inhibitor & its concentration	Free energy of adsorption G_A^o in KJmol^{-1} (Entropy of adsorption, S_A^o in Jmol^{-1})				Q_A (307-327 K) in KJmol^{-1}	
	Temp. (K)	297	307	317		327
ANS (0.1%)		-23 (461.3)	-27.4 (460.6)	-19.4 (800)	-14.4 (582.2)	-226
o-TNS (0.4%)		-24.6 (75.0)	-25.4 (75.0)	-27.5 (216.1)	-25.3 (222.3)	-27
o-HNS (0.4%)		-23.1 (404.4)	-27.2 (404.6)	-13.6 (1358)	-17.3 (367.9)	-179

From the results it is evident that for all the three inhibitors, the heats of adsorption are negative. The values of free energy of adsorption are also negative, which suggests a

strong interaction of the inhibitor molecules and spontaneous adsorption of the metal surface^{22,23}. The G_A^o values for o-TNS inhibitor, like its inhibitive efficiencies, are almost the same (-24.3 KJmol⁻¹ to -27.5 KJmol⁻¹). The positive values of the entropies of adsorption, S_A^o , also suggest the adsorption to be spontaneous process.

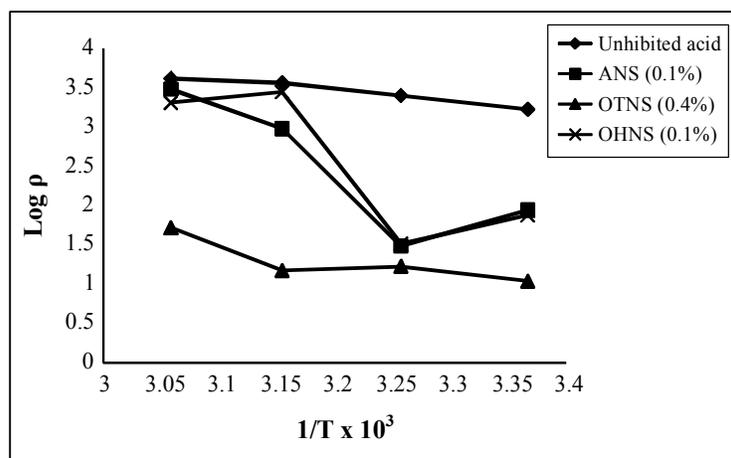
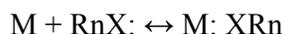


Fig. 2: Plot of corrosion rate Vs temperature

Mechanism of Inhibition

From the weight loss data, the result also show that the incorporation of CH₃ or -OH group in o-position in aniline part of the Schiff base has a deleterious effect on the inhibitive efficiency of ANS. In most of the organic corrosion inhibitors are compound with at least one polar unit having atoms such as nitrogen, sulphur and oxygen. The polar unit is regarded as the reaction center 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 center 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.



According to Aramaki et al.²⁴ 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 principle. The bulk metal is classified as the hard acid and a molecule or ion of the soft base forming a stable donor acceptor bond. The adsorbed monolayer will then block the

dissolution of the metal ions. The size, orientation, shape and electric charge on the molecule determine the degree of adsorption and hence the effectiveness of the inhibitor. The six membered rings are the most stable for chelates with contain one or more double bonds. In the present study Schiff bases derived from some ortho substituted anilines and salicylaldehyde have been reported as corrosion inhibitors for Aluminium in HCl acid due to the presence of an imine ($-C=N-$) group and conjugated double bonds with polar units (CH_3 or $-OH$).

CONCLUSION

The corrosion of aluminium in hydrochloric acid containing different ortho substituted aniline-N-salicylidene has been studied with respect to inhibitor concentration, period of exposure and temperature. At 0.4% inhibitor concentration in 1 N acid, the order of efficiency is –

$$o\text{-HNS (38.81\%)} < \text{ANS (98.7\%)} < o\text{-TNS (99.36\%)}$$

At 0.1% inhibitor concentration in 1 N acid, the order of efficiency is –

$$o\text{-TNS (54.99\%)} < \text{ANS (94.8\%)} < o\text{-HNS (95.49\%)}$$

The activation energies are higher in inhibited than in uninhibited acid. It appears that an efficient inhibitor is characterized by a relatively greater decrease in the free energy of adsorption. The inhibitors appear to function through adsorption due to the presence of the imine ($-C=N-$) group and conjugated double bonds

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