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The Potential of Benzotriazole in retarding corrosion rate of Aluminium in Acid media.

Arvind Kumar Singh (Senior Professor)[1], Shailendra Kumar Singh[2], Sarfaraz Nawaz[3], Satyendra Sharma[4]

[1]*Department of Chemistry cum Corrosion Laboratory, Faculty of Science, V.K.S.University, Ara*
[2]*Reseach Scholar, Department of Chemistry, Faculty of Science, V.K.S.University, Ara*

Abstract: **The corrosion inhibition potential of benzotriazole (BTA) on aluminium in 0.25M hydrochloric acid (HCl) was investigated using potentiodynamic polarization techniques. The study revealed that BTA acts as a mixed-type inhibitor, significantly reducing the corrosion rate of aluminium by adsorbing onto its surface. The inhibition efficiency increased with higher BTA concentrations, reaching up to 78.3% at 1.8×10^{-4} M. Adsorption behavior followed the Frumkin isotherm, indicating interactions between adsorbed inhibitor molecules. The calculated standard free energy of adsorption (ΔG°_{ad} = -12.9 kJ/mol) suggested a physisorption mechanism, primarily driven by electrostatic interactions between protonated BTA and the negatively charged aluminium surface. The findings highlight BTA's effectiveness as a corrosion inhibitor for aluminium in acidic environments, with implications for industrial applications.**

Keywords: **Benzotriazole (BTA), Aluminium corrosion, Acid inhibition, Potentiodynamic polarization, Frumkin isotherm, Physisorption, Hydrochloric acid (HCl), Corrosion inhibition efficiency, Mixed-type inhibitor, Electrochemical adsorption.**

I. INTRODUCTION

Aluminium has a remarkable industrial importance and material for engineering technology. Owing to its high thermal and electrical Conductivity, low cost and light weight. The resistance of aluminium against Corrosion in acid media can be attributed to a rapidly formed Compact, strongly adherent invisible Protective oxide film on its Surface. Therefore, aluminium has been Known to exhibit widely different electrochemical properties in different aqueous electrolytes, such that aluminium and its alloys are widely used in many industries such as chemical batteries, pipes and reaction vessels. The widely used HCl acid solution in this medium, which has induced a great deal of research on aluminium. So, the best method for metal protection from corrosion is the use of effective organic inhibitor containing hetero atoms such as (N, O, S) or structures containing pair of electrons on the central atom in their molecules through which they can absorb on the metal surface. Generally, the adsorption of this inhibitor on metal surface depends on the nature and surface charge of the adsorbent, the chemical structure of the adsorbate and the type of electrolyte solution.

Physisorption and chemisorption are the principal types of interaction between adsorbate and adsorbent. The physisorption is weak absorption and its chemisorption is stronger. It is the result of electrostatic attractive forces between inhibiting organic ions or dipoles and electrically charged metal surface. Physisorption involves rapid interaction between adsorbent and adsorbate but it is also easily removed from surface with subsequent rise in temperature. In the chemisorption, strong,coulombic forces lead the interaction between adsorbate and adsorbent and involve charge transfer from the adsorbate to the adsorbent in order to form a coordinate or covalent type of bond out of adsorption. The process can be described by several types of adsorption isotherms such as Langmuir, Freundlich, Temkin and Frumkin. In the present study benzotriazole inhibitor was used for corrosion inhibition of aluminium in 0.25M HCl using potentiodynamic polarization. Adsorption study was made at various temperature and nature of isotherms were studied in the collaboration of corrosion rate study as well as its inhibition by benzotriazole during the result obtain by polarization study.

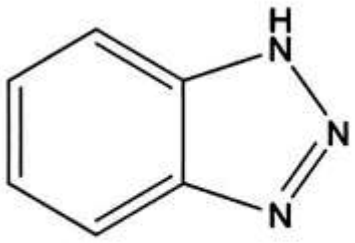

Figure 1. Chemical molecular structure of 1, 2, 3-benzotriazole.

II. EXPERIMENTAL

The working electrode employed in this work was made of aluminium (99.99%) locally available. For electrochemical measurements, the investigated materials cut as rectangular holed pieces of geometric surface area (1"* 1"), Welded with as-wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite to offer an active flat disc shaped surface of (1 square inch).

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Geometric area, to contact the test solution. Priorto each experiment, the exposed area of the aluminium electrode was abraded with 800, 1200, 1500, and 2000 grades of emery papers. The electrode was then rinsed with acetone, distilled water, and finally dipped in the electrolytic cell. The electrochemical measurements were performed in a typical three compartment glass cell consisting of the aluminium specimen as working electrode, platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrochemical experiments were performed.

Each run was carried out in aerated solutions at the required temperature, using a water thermostat. All potentials given in this work are referred to this reference electrode (SCE). The electrode was immersed in test solution at open circuit potential (OCP) for 30 minutes at 30^0C before starting the measurements to be sufficient to attain a stable state.

III. Results And Discussion

Potentiodynamic polarization measurement

The polarization behaviour of aluminium electrode in 0.25M HCl solution in the absence and presence of different concentrations of benzotriazoles at 30^0C are presented in fig:2. It is clear that both the inhibitor works as mixed corrosion inhibitor affecting anodic and cathodic both the reactions.

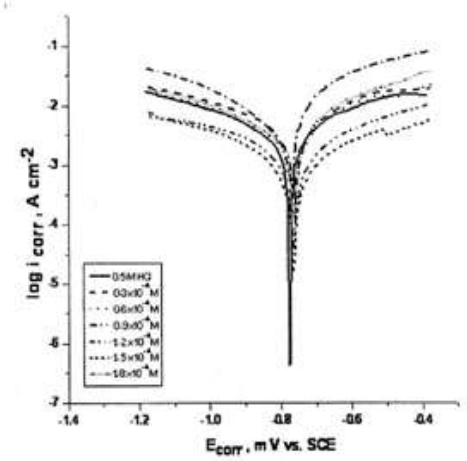

Figure 2. Potentiodynamic polarization curves for the corrosion of aluminium in 0.5 M HCl in absence and presence of different concentrations of 1, 2, 3, benzotriazole at 30°C.

The measured free corrosion potential used for this study was found to be-776 mv for aluminium in 0.25M HCl. It is found that the free corrosion potential for aluminium in 0.5M HCl is -785.1 mv. It is found that the free corrosion potential for aluminium in 0.05M HClas -820 mv and found it to be -980 mv for aluminium in 2.0M HCl.

From these results, we can conclude that the free corrosion potential depends on both the composition of the electrode and the concentration of electrolyte used. The electrochemical parameters including corrosion current densities (Icorr). Corrosion potential (Ecorr), cathodic and anodic total slopes (bc&ba) and corresponding inhibition efficiency (%I.E_{pp}) and surface coverage (**θ**) were calculated according to the following equations.

$$\%\ IE_{PP} = \left[\frac{i_b - i_{inh}}{i_b}\right] \times 100 \quad \ldots\ldots\ldots\ldots\ 1$$

$$\theta = \left[\frac{i_b - i_{inh}}{i_b}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Wherei_b and $i_{inh}$are the corrosion current densities in the absence and the presence of the inhibitor, respectively. It is clear that i_{corr} decreases with increasing the inhibitor concentration, due to the increase in the surface coverage of the electrode surface by adsorption.

Adsorption isotherm & standard adsorption free energy (ΔG_{ads}).

In order to get more information about the type of adsorption of benzotriazole inhibitor on the surface of aluminium at different concentrations of inhibitor, the data obtained from polarizationcurves have been tested with several adsorption isotherms including Langmuir and Frumkin. “Frumkin” adsorption isotherms were found to fit well with the experimental data. The adsorption isotherm relationship of the Frumkin is represented by the following equation.

$$[\frac{\theta}{(1-\theta)}]\exp(-2a\theta)=KC$$

Or its linear form:

$$ln[\frac{\theta}{(1-\theta)}]=\ln K + 2a\theta$$

Where (**θ**) is the surface coverage (c) is the inhibitor concentration in the bulk of solution, (a) is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface (it is a measure for the steepness of the adsorption isotherms)and (k) is the equilibrium constant of the adsorption reaction. Plotting of **θ** against log C resulted to a s-shape curve and is represented in fig-3(a), this is indicating that the adsorption of inhibitor follows Frumkin isotherm. On the other hand, by plotting ln[**θ/(1-θ)C**] versus **θ** for Al in 0.25M HCl containing various concentrations of inhibitor straight lines which has been shown and represented in fig3(b). The linear fitting slope for the Frumkin isotherm gave the value of (a) which equals 1.26 and the intercepts gave the value of of (k) which equals 2.9936 M^{-1} for the investigate inhibitor.

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The higher K value (>100M^{-1}) indicates the formation of the stronger and more stable adsorbed layer which is the result of the higher inhibition efficiency. Also, the positive value of (a) imply that the interaction between molecules causes an increase in the adsorption energy with the increase of (θ).

K is related to the standard free energy of adsorption (ΔG^{o}_{ads}) as shown in the following equation,

$$K=\frac{1}{55.5}\,exp(-\frac{\Delta G ads}{RT})$$

Where K is the value of the concentration of pure water which is 55.5M. R is the universal gas constant and T is the absolute temperature.

It can be observed that the value of ΔG^{o}_{ads} for benzotriazole inhibitor is negative. Actually, this shows the spontaneity of the adsorption process and the stability of the adsorbed layer on aluminium surface. It is known that the value of $\Delta G^{o}_{ads}$of the order – 20kj/mole or lower indicate a physisorption, those of the order -40KJ/mole or a transfer from the inhibitor molecules to the metal surface to form a coordinate or covalent type of bond, Chemisorption. The value of $\Delta G^{o}_{ads}$of the investigated benzotriazole was -12.9 KJ/mole at 30^{o}C. This indicates that the adsorption of the investigated benzotriazole on aluminium surface is typical physisorption.

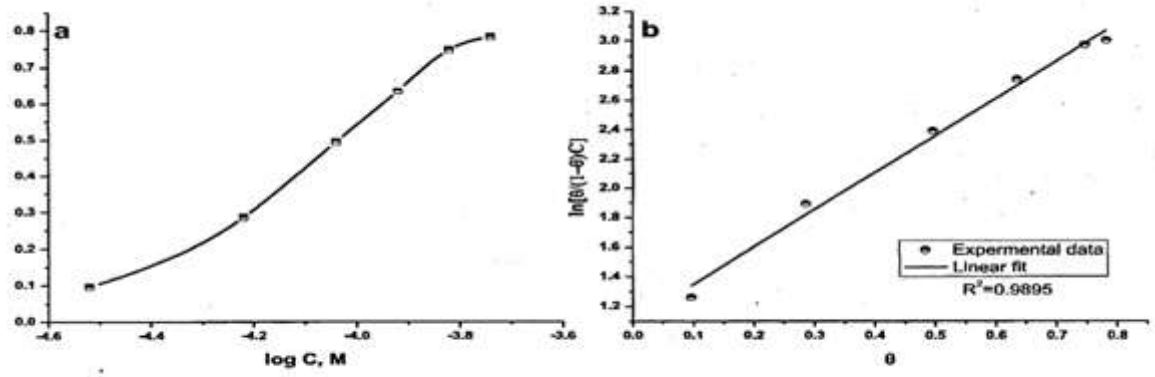

Figure-3(a) Frumkin adsorption isotherm of investigated 1, 2, 3-benzotriazole on aluminium surface in 0.25 M HCl solution at 30o C. (b)The linear form of Frumkin adsorption isotherm.

IV. Mechanism Of Corrosion Inhibition

The adsorption of the studied compound can be attributed to the presence of polar unit having lone pair of electrons on nitrogen / aromatic heterocyclic rings. Therefore, the possible reaction centre are lone pair electrons on hetro-atoms and π –electrons of aromatic rings. The adsorption and inhibition effect of studied compound in 0.25MHCl solution can be explained as follows: -

In aqueous acidic solutions BTA exists either as neutral molecules or as protonated molecules and may adsorb on the metal/acid solution interface by the following way: -

(1) Electrostatic interaction of protonated molecules with already adsorbed chloride ions.
(2) Donor –acceptor interactions between the π –electrons of aromatic sing and vacant p-orbital of surface aluminium atoms.
(3) Interaction between unshared electron pairs of heteroatoms and vacant p-orbital of aluminium surface atoms.

In general, two ways of adsorption are considered on the metal surface in acid media. In the first mode the neutral molecules may be adsorbed on the surface of aluminium through the chemisorption mechanism, involving the displacement of water molecules from the aluminium surface and the sharing lone pair of electrons between the hetero-atoms and aluminium. The BTA can also adsorb on the aluminium surface on the basis of donor-acceptor interactions between π –electrons of the aromatic ring and vacant p- orbitals of surface aluminium atoms. In the second ways, the aluminium surface bears +ve charge in acid solution, it is difficult for the protonated molecules to approach the +vely charged Al surface due to electrostatic repulsion. Since chloride ions have a smaller degree of hydration, thus they could bring excess

–ve charges in the vicinity of the interface and is pertinent to more adsorption of the +vely charged molecules, the protonated BTA adsorb through electrostatic interaction between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed Cl^{-} ions and protonated benzotriazole.

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It can be concluded that the inhibition of aluminium corrosion in 0.25MHCl is mainly due to the electrostatic interaction. The decrease in inhibition efficiency with rise in temperature supports the theory of electrostatic attraction.

V. CONCLUSION

The corrosion inhibition of aluminium by BTA was studied by electrochemical measurements and results show that –

The inhibition efficiency of Benzotriazole in 0.25M HCl solution increases with increasing its Cone^{n}. The inhibitor acts as mixed type inhibitor. The adsorption of the inhibitor obeys the Frumkin adsorption isotherms. The calculated value of Gas indicated that the adsorption of inhibitor molecules on the aluminium surface is typical physisorption.

Table-1
Potentiodynamic Polarization Parameters for the Corrosion of aluminium in 0.25m HCl containing different concentrations of Benzotriazole at 30^0C.

Invisitor cone M	Ecoss. mv.	Icarr. BA cm^{-2}	Bam v dec^{-1}	Bam v dec^{-1}	Q.	I.Epp
0	775	590	302	245	….	….
0.3×10^{-4}	765	535	301	286	0.096	9.7
0.6×10^{-4}	763	420	316	206	0.285	28.5
0.9×10^{-4}	771	298	314	218	0.495	49.5
1.2×10^{-4}	764	212	326	230	0.634	63.6
1.5×10^{-4}	762	140	328	260	0.746	74.6
1.8×10^{-4}	756	124	337	252	0.784	78.3

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