STUDIES OF SOME AROMATIC COMPOUNDS FOR CORROSION INHIBITION OF ALUMINIUM IN ACIDIC MEDIUM

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Abstract:

The aim of this work is to investigate corrosion inhibition characteristics of Aluminium inHydrochloric acid (0.1N) in presence of different concentration (0.2, 0.4% and 0.6%) of two inhibitors namely p-Nitrophenol and Nitrobenzeneusing Tafel polarization studies and weight loss methods. Open circuit potential, inhibition efficiency, corrosion current and corrosion rate have been determined in the absence and presence of inhibitors at different concentrations such as 0.2, 0.4% and 0.6% .It is observed that the inhibition increases with the increase in concentration of the inhibitors in acidic media. The experimental data showed that the the maximum inhibition performance could reach about 72-78% at the concentration of 0.6%. The inhibition efficiency of the p-Nitro phenol is found to be higher than that of Nitrobenzene.

Keywords **-** Aluminium, inhibitors, Inhibition efficiency, Tafel plot, Weight loss

I INTRODUCTION:

Aluminium is the third most prevalent element and the most abundant metal in the earth's crust, representing approximately 8% of total mineral components.[1]The most important feature of aluminium is its high strength to weight ratio. Its high electrical and thermal conductivity, in addition to its relatively low price, make aluminium very attractive in various applications.[2] In terms of corrosion, aluminium by itself is not resistant, however if an oxide layer is formed on the surface, it becomes highly resistant to corrosive attack in various media. However, when exposed to acidic, alkaline, and chloride-containing media, the oxide layer is damaged, exposing the Aluminium materials to the attack of the corrosive environment.[3- 4]The acidic solutions are usually used in metal industries for de-scaling, acid pickling; cleaning process and presence of these corrosive media are the foremost reasons for the increase in the rate of metallic dissolution. Corrosion is the result of the interaction between the metal and environments, leading to its destruction gradually, so corrosion is the deterioration of metal forming chemical attack or interacts with its environment. It is permanent and persistent problem often cannot be eliminated completely. Prevention is more realistic and achievable than the total elimination; require a corrosion inhibitor to prevent corrosion of metals. [5-6]

Corrosion inhibitors are substances that, when added in small concentrations to corrosive media decrease or prevent the interaction of the metal with the media. Compounds with ∏bonds generally exhibit marked inhibitive properties due to the interaction of ∏ -orbital with the metal surface[7-8]. Most of the well-known acid inhibitors in acid are organic compounds holding sulphur, oxygen and nitrogen atoms. The effectiveness of these molecules mainly depends on their ability to get adsorbed on the surface of metal particularly through polar groups. Most effective inhibitors are used to contain a homogenous such as O, N, S and multiple bonds in their molecules by which they stepped on the metal surface Significant amount of effort is devoted to develop efficient and novel corrosion inhibitors, in recent years[9-10]. Various compounds containing nitrogen, sulphur, and/or oxygen, especially certain amino derivatives have attracted more and more attention in this area. The present investigation was undertaken to examine the corrosion inhibition efficiencies of two inhibitors such as p-Nitrophenol and Nitrobenzene, on Aluminium in 0.1N HCl solution using gravimetric weight loss measurements, polarization studies.. It has been found that these inhibitors are effective in acidic medium and that this effectiveness increases with increase in the concentration (in the studied range of concentration.)

II MATERIALS AND METHODS

2.1 Inhibitor and solutions

All chemicals used were of analytical grade .The aggressive solutions of 0.1N HCl was prepared by using standard grade HCl (Merck)and deionized water. Solutions of inhibitors (P-Nitrophenol and Nitrobenzene) of different concentrations (0.2, 0.4 and 0.6%) were prepared either in distilled water or in ethanol.

2.2 Gravimetric method

weight loss experiments were carried out using rectangular specimens of aluminum (99.9% purity) having dimension 3×2×0.16 cm^3 and a small hole of about 3 mm diameter near the upper edge for the purpose of hanging. They were polished with emery papers and washed with benzene, distilled water and finally with acetone and then dried in oven at 60 ^oC for about half an hour. They were then kept in a desiccator, cooled down to room temperature and then weighed accurately using a digital balance. They were subjected to further heating, cooling and weighing until a constant weight was obtained. Mass loss experiments were performed in 0.1 N HCl acid in the presence of, 0.2, 0.4, 0.6% concentration of inhibitors. The metal specimens were immersed in the aggressive medium for 24 hour at room temperature with a periodical evaluation of the corrosion rate. Each specimen was suspended by a glass hook and immersed in a beaker containing 100 mL of the test solution at room temperature. Later, the test specimen was cleaned with distilled water, dried in an oven for 20 min and finally weighted. Similar experiments were carried out in acid solutions with inhibitors. Stock solutions(10%)of p-Nitrophenol and Nitrobenzene were prepared and diluted to get different concentrations(0.2 to .6%. The experiments were carried out in duplicate and the average values were reported. The rate of corrosion was determined by the following equation .[11-12]

$$\text{Corrosion rate (mpy) R} = \frac{(K\Delta W)}{DAT} \qquad (1)$$

Where R = corrosion rate (mpy), W= weight loss (g), A= surface area of metal specimen (cm2), t= time of treatment (h), D= density of specimen (g/cm3), and K= constant .The inhibition efficiency (η %) was obtained by the following equation:

$$\text{Inhibition Efficiency}(\eta)\% = \frac{100\,(\Delta M_u - \Delta M_i)}{\Delta M_u} \qquad (2)$$

Where ΔM_u and ΔM_i are weight loss without and with inhibitors.

2.3 Electrochemical studies

Electrochemical studies were executed using three-electrode cell assembly consisting of aluminium as working electrode (exposed area 1cm^2), platinum electrode as counter electrode (1cm^2) and saturated calomel electrode (SCE) as reference electrode at room temperature. For acid corrosion, the working area of metal specimens was made to contact with the electrolyte for 60 min preceding the experiment. [13]

Polarization method

For polarization study, the specimen aluminum plate used in corrosion inhibitor studies was covered with a teflon tape so as to have a total surface area of 1 cm^2. It was then exposed to corrosive solution (0.1N HCl) and used as a working electrode. It was polished by using emery paper with a polisher and degreased by acetone prior to use. Standard working potentiostat was used for polarization studies, with and without inhibitor in 0.1N HCl. The test solutions were prepared in doubly distilled water. Solutions of inhibitors of different concentrations (0.2, 0.6 and 0.4%) were prepared either in distilled water or in ethanol. The platinum foil was used as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The electrochemical experiments were performed by applying varying current in both the cathodic and anodic directions. Finally, in the experimental cell, the working electrode was let free until the stationary open circuit was reached. By changing potential, the corresponding change in current was obtained. First cathodic and then anodic polarization data were recorded. As per standard procedure [14-16] the corresponding polarization curves were then drawn from the recorded observation. The value of the corrosion current (I_{corr}) and potential was obtained from the intersection of cathodic and anodic Tafel lines. Slope analysis of Tafel curves gave the corrosion current and the inhibition efficiency (η %) and corrosion rate (in mpy-mils per year) were calculated by the following equations.

$$\text{Inhibition Efficiency } (\eta) = \frac{[I_{corr(blank)} - I_{corr(inhib.)}] \times 100}{I_{corr(blank)}} \quad (3)$$

$$corrosionrate = \frac{0.1288 \times I_{corr} \times Eq.Wt(Al)}{Area \times Density\ (Al)} \quad (4)$$

Where I_{corr} and I'_{corr} are corrosion current of the working electrode in the absence and presence of inhibitors.

III RESULTS AND DISCUSSION

In general, highly pure aluminum metal is more corrosion resistant than the commercially pure aluminium. Aluminium corrodes more rapidly both in acidic as well as in alkaline medium as compared with distilled water. When aluminum dissolves anodically both $A1^{3+}$ and $A1^{+}$ are formed initially. The univalent ion then reduces H_2O to form the trivalent ion in accordance with following equations.

$$Al \rightarrow Al^{3+} + 3e^{-} (E^0 = -1.7\ volt)$$

$$Al \rightarrow Al^{+} + e^{-}$$

$$Al^{+} + 2H_2O \rightarrow Al^{3+} + H_2 + 2HO$$

When aluminium is anodized, H_2 is evolved at the anode and cathode. Hydrogen evolution at the anode can be explained by increased local action corrosion during anodic dissolution. In acidic solution, the overall reaction during the corrosion of the Al is given as:

$$2Al + 6H^{+} \rightarrow 2Al^{3+} + 3H_2$$

Thus, to protect the metal from corrosion, inhibitors have been added and their effects are studied. In the present work, Nitro benzene and p-Nitro phenol two compounds have been used as corrosion inhibitors and their effects are studied in acidic medium employing Tafel intercept polarization method and weight loss method to investigate the inhibitive action of these aromatic inhibitors on corrosion of Al metal. The corrosion parameters such as corrosion current (I_{corr}), corrosion-rate and inhibition efficiency for these inhibitors are determined at their different concentrations and the results are tabulated in Table 1and 2.

3.1 Gravimetric corrosion inhibition studies

The corrosion inhibition efficiencies and corrosion rate of two aromatic compounds p-Nitrophenol and Nitrobenzene for 24 h at room temperature are listed in Table 1. Both molecules displayed excellent inhibition efficiency on Aluminium surface, maybe due to the presence of highly polarizeable Nitrogen atom in the aromatic ring. Presence of p-Nitrophenol linkage and Nitrobenzen aromatic rings increases its inhibition efficiency even at very low concentration. For a period of 24 h, p-Nitrophenol showed higher inhibition efficiency than Nitrobenzene. In addition to this highly delocalized ∏ electron cloud of the aromatic ring increases its inhibition efficiency. Even though there is a structural similarity between Nitrobenzene and p-Nitrophenol , corrosion inhibition efficiency of Nitrobenzene is relatively low, compared to that of p-Nitro-phenol which may be due to the deviation from co planarity of the molecule. [17-24]

Table 1: Gravimetric corrosion inhibition efficiencies(η) and corrosion rate of p-Nitrophenol and Nitrobenzene on Al in 0.1N HCl for 24 hr at room temperature

Inhibition Concentration (%)	p- Nitrophenol		Nitrobenzene	
	Corrosion Rate	Inhibition Efficiency (η),%	Corrosion Rate (mpy)	Inhibition Efficiency (η),%
0.2	46.03	51.78	61.37	35.71
0.4	35.23	63.09	48.87	48.80
0.6	27.27	71.42	29.55	69.04

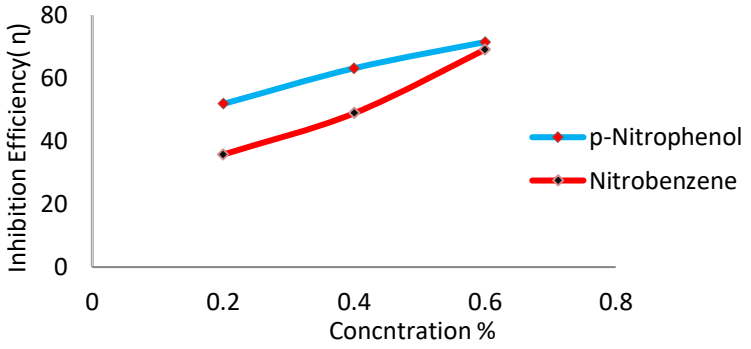


Fig. 1. Variation of corrosion inhibition efficiencies of p-Nitrophenol and Nitrobenzene with concentration on Al in. 1N HCl

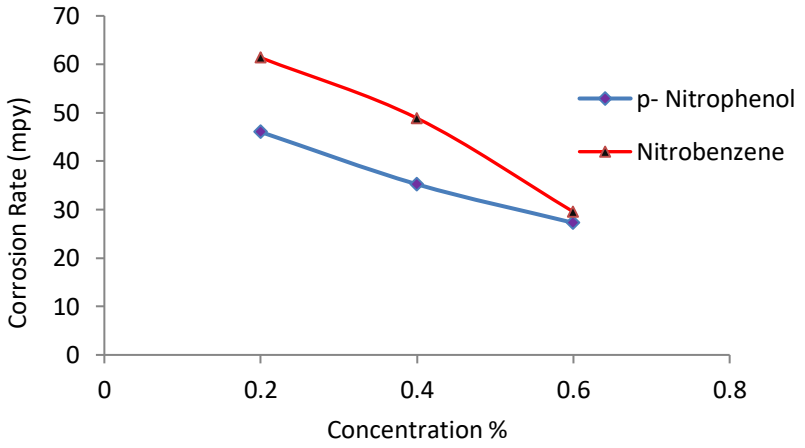


Fig. 2. Variation of corrosion rate of Al with concentration of P-Nitro- phenol and Nitrobenzene in 0.1NHCl

Figures.1 and 2 represent the variation of corrosion inhibition efficiency and corrosion rate with concentration for the inhibitors molecules at concentration of .2% to 0.6%.The plots reveal that the decrease of corrosion rate with increase inhibitor concentration and inhibition efficiencies (η) increase with concentration of inhibitor. This may be due to excellent adsorption of these molecules on the metal surface because of the presence of highly active heteroatom and slow hydrolysis rate of these molecules in acidic medium. From the results of gravimetric corrosion studies, one can reach into the conclusion that p-Nitrophenol and Nitrobenzene molecule acts as good corrosion inhibitors.

3.2 Polarization measurements

Potentiostatic method has been employed for polarization measurement. When a DC potential is applied from an experimental source to a metal undergoing corrosion in contact with a solution, a net current I flows through the metal. This current is due to the difference between partial current due to cathodic reaction (Ic) and anodic reaction (Ia) of the metal dissolution. These currents are due to cathodic and anodic reactions respectively. Graphs are plotted between potential vs logarithm of current (Tafel Plots). The complete Tafel polarization curves are shown in Fig.3(.a,b,c.).Cathodic and anodic polarization curves give cathodic Tafel and anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines give the corrosion current (I_{corr}) and potential [25- 30]. The kinetics of the anodic and cathodic reactions occurring on Aluminium electrodes in 0.1N HCl solutions with different concentrations of inhibitors (.2% to 0.6%) was studied through the polarization measurements.

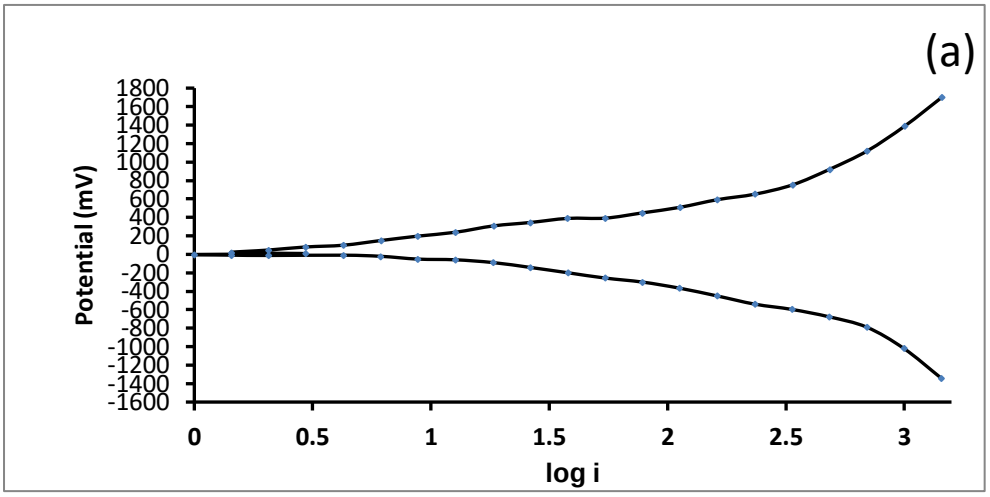
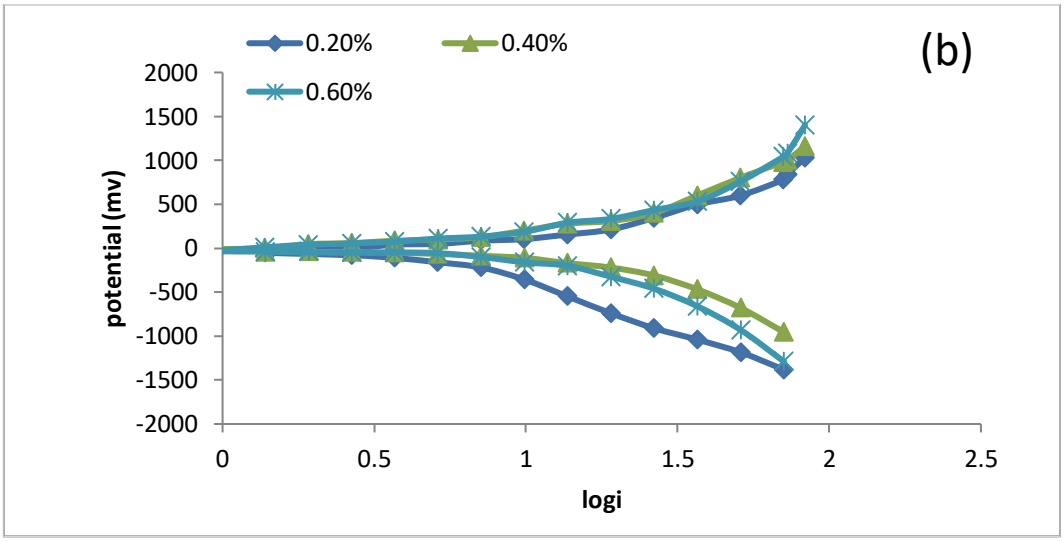


Fig 3- (a)Tafel plot for Al in 0.1 N HCl without inhibitor



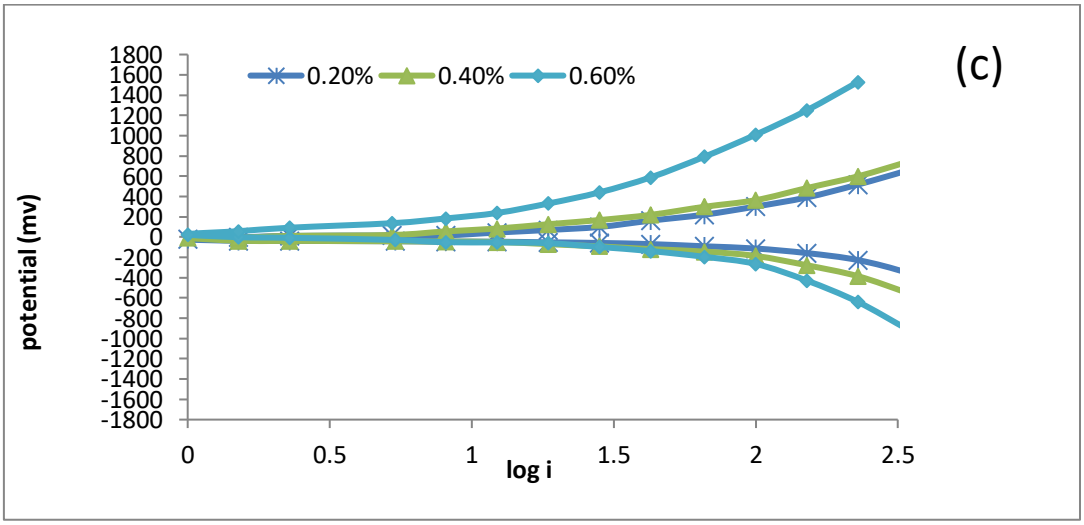


Fig 3- (b) Tafel plots in presence of Nitro benzene and (c) in presence of p-Nitro phenol

The results of electrochemical corrosion parameters, i.e. corrosion current (i_{corr}), Inhibition Efficiency (η) and corrosion rate regrouped in Table 2 were collected from Tafel plots and polarization experiments obtained under uninhibited and inhibited conditions. The corrosion rate is calculated by applying the Tafel polarization method.

Table 2: Polarization corrosion inhibition efficiencies (η) and corrosion rate of p-Nitrophenol and Nitrobenzene on Al in 0.1N HCl for 24 hr at room temperature

Inhibition Concentration (%)	p- Nitrophenol			Nitrobenzene		
	I_{corr} mA	Corrosion Rate (mpy)	Inhibition Efficiency (η),%	I_{corr} mA	Corrosion Rate (mpy)	Inhibition Efficiency (η),%
Blank	243.78	260		243.78	260	
0.2	104.23	111.09	57.14	138.99	148.14	42.14
0.4	99.78	106.35	59.06	108.39	115.52	55.53
0.6	52.48	55.93	78.47	65.52	70.90	72.71

It is observed from the Table 2 that the presence of p-Nitro phenol and nitro benzene decreases the corrosion rate for aluminum. In case of p-Nitro phenol, the value for η is found maximum (78.47%) at its higher concentration (0.6%), whereas minimum change in η values is noticed with increase in inhibitor concentration for p-Nitrophenol (from 57.14% to 78.47%). Both the inhibitors inhibit the corrosion of aluminum to a maximum extent at the concentration of 0.06% (by weight). It is also observed that the inhibitive effect of p-Nitrophenol on the corrosion of aluminum was maximum at its higher concentration (η=78.47% at 0.06%) which is more as compared to that of nitro benzene (η=72.71% at 0.6%). As the Tafel intercept polarization method is more sensitive, the results obtained by this method clearly indicate that the corrosion rate for aluminum in presence of p-Nitro phenol decreases with increase in its concentration from 111.09 mpy to 55.93 mpy. In case of nitro benzene the corrosion rate is observed to change from 148.14 mpy to 70.90 mpy with increase in its concentration from 0.2 % to 0.6 %. Thus, p-Nitro phenol can be considered more corrosion protective. It is also observed that the inhibition efficiency of the p-Nitro phenol is more as compared to Nitro benzene. The percentage inhibition efficiencies for aluminium are determined at different concentrations (by weight) of inhibitors, viz. 0.2, 0.4 and 0.6%. The protective behavior of both the inhibitors (by both the methods) is observed the best at their higher concentration. The Icorr and mass loss values decrease with the increase in concentration of the inhibitors. The inhibition efficiency is found to increase with increasing concentration of inhibitors in acidic (0.1N HC1) medium. The inhibition efficiencies obtained by weight loss measurements are in good agreement with values given by the Tafel method. The trend of the results so obtained from both the methods is found to be in good agreement with each other.

VI CONCLUSION

The aromatic compounds under study are good inhibitors in acidic medium for aluminium. The inhibition efficiency of both aromatic compounds was exceeded from 72% to 78% which may be due to the presence of lone pair of electrons on N atom and aromatic rings etc; All corrosion monitoring studies revealed that the inhibition efficiency of Nitrobenzene is lower than that of p-Nitrophenol at all concentrations. The maximum inhibition efficiency was observed in case of p-Nitro phenol. It can be concluded that p-Aminophenol is more protective than Nitrobenzene for corrosion of Aluminium in acidic media.

V ACKNOWLEDGMENT

The author is thankful to HOD department of Chemistry, JNV University, Jodhpur for providing research facilities.

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