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Studies on Thiourea Derivatives as Corrosion Inhibitor for Aluminum in Sodium Hydroxide Solution

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Abstract: Aluminum is actually a very active metal, meaning that its nature is to oxidize very quickly. While a weakness for most metals, this quality is in fact the key to its ability to resist corrosion. When oxygen is present (in the air, soil, or water), aluminum instantly reacts to form aluminum oxide. This aluminum oxide layer is chemically bound to the surface, and it seals the core aluminum from any further reaction. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are potential corrosion inhibitors. In present study the inhibition efficiency of thiourea, phenyl thiourea (PTU) and 4-carboxy phenyl thiourea (CPTU) in 0.3, 0.4, 0.6 and 1.0M NaOH solution has been calculated by weight loss measurements. It was found that the corrosion of aluminum in NaOH solution was considerably reduced in presence of such inhibitors. Thiourea forms a protective film on the surface of metal through adsorption. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosive media. Our aim of this work is to study the corrosion behavior of Aluminum in aqueous sodium hydroxide solutions of different concentrations and inhibition activity of some thioureas derivatives.

Key words: Aluminum, Corrosion inhibition, Thiourea derivatives, NaOH.

INTRODUCTION

The corrosion resistance of aluminum is dependent upon its protective oxide film. This film is stable in aqueous media when the pH is between about 4.0 and 8.5. The oxide film is naturally self-renewing and accidental abrasion or other mechanical damage of the surface film is rapidly repaired. From a purely thermo dynamical point of view aluminum is active. However, in oxygen containing environment (air, water), aluminum is rapidly covered with a dense oxide layer[1]. The oxide layer is essentially inert, and prevents corrosion. If the oxide film is damaged, e.g. by a scratch, new oxide will immediately form on the bare metal[2]. This way aluminum is given excellent corrosion protection. Aluminum posseses attractive properties like high negative potential and high energy density in alkaline media. The reaction readily occurs even at room temperature, yielding hydrogen and sodium aluminates:

$$2Al + 2NaOH + 6H_2O \rightarrow 2Na\,[Al\,(OH)_4] + 3H_2. \qquad (1)$$

It should be noted that the structure and behavior of aluminates ions in alkaline solutions have been studied in detail. In dilute solutions, the stable Al species are monomer tetrahedral aluminates ions $[Al(OH)_4]^-$ and their dimers stabilized by cations present in solution.

Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are potential corrosion inhibitors. While extensive investigations have been carried out on inhibitor properties of thiourea, due attention has not yet been paid to a systematic study of inhibitor action of thiourea derivatives. However, several substituted thiourea have been investigated as corrosion inhibitors[3]. Corrosion inhibition properties of phenylthiourea polymers on aluminium in alkaline medium have recently been published[4].

Most of the effective organic inhibitors used in industry have heteroatoms such as O, N, S containing multiple bonds in their molecules through which they can adsorb on the metal surface[5-8]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair determines the adsorption of these molecules on the metal surface.

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MATERIALS AND METHODS

Experimental:

Alloy Used: Commercially available aluminum sheet was used for all experiments. The aluminum sheet of 2 mm thickness was mechanically press-cut into 3 × 3 cm coupons.

Specimen Preparation: The aluminum coupons were made the surface even and smooth. The specimens were then washed and degreased with acetone.

Chemicals Used: Analytical reagent (AR) grade sodium hydroxide NaOH was used to prepare aqueous solution of concentrations 0.3, 0.4, 0.6 and 1.0 M, distilled water was used for the preparation of all solutions. Analytical reagent grade thiourea and laboratory synthesized derivatives Phenyl thiourea (PTU) and 4-carboxy phenyl thiourea (CPTU) were used to estimate the corrosion inhibition efficiency. 0.2% w/v concentration of inhibitors was used for inhibition studies.

Weight Loss Studies: Wight loss studies were carried out at room temperature (21°C). The aluminum coupons were weighed and surface area of all the samples were calculated before the weight loss studies. The aluminum coupons were immersed in 100 ml test solutions of sodium hydroxide of different concentrations. The weight loss studies were carried out for 15, 30, 45, 60, 75 and 90 minutes.

Corrosion rates (weight loss per cm^2 per hour) were calculated using following expression[9].

$$\text{Corrosion rate } (g.cm^{-2}h^{-1}) = \frac{W_1 - W_2 \text{ (g)}}{\text{Surface area } (cm^2) \times \text{Time (h)}}$$

Where,
W_1 = initial weight of coupon
W_2 = weight of coupon after treatment
$W_1 - W_2$ = weight loss (g)
The percentage inhibition efficiency (IE %) of the thiourea derivatives was calculated from corrosion rate values by using the following equation:

$$\%\text{ I.E.} = \frac{W_{blank} - W_{inhibitor}}{W_{blank}} \times 100$$

Where, Wblank and Winhibitor are the corrosion rates in absence and presence of the inhibitor respectively.

RESULTS AND DISCUSSION

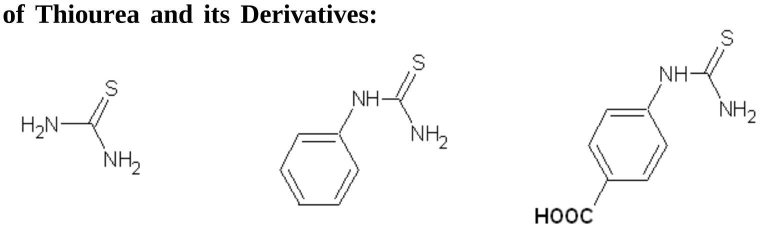
Weight Loss Studies:

Reaction Kinetics: Figure 1 shows the plots of weight loss of aluminum in g/cm^2 with the exposure time (in minutes). The graph reveals that the weight loss increased with increasing concentration of the sodium hydroxide solution. In initial period of exposure, the weight loss is very little and gradually increased with time. It is due to the fact that the aluminum oxide layer present on the metal surface protected the metal against the corrosion at initial stages of exposure. It has also been investigated that the oxide layer is non protective above pH 9[10]. As soon as the oxide layer is dissolved the reaction became more vigorous. The reaction that occurs between the aluminum and the sodium hydroxide is

$$2Al(s) + 2NaOH\ (aq) + 6H_2O\ (l) \rightarrow 2Na\ [Al\ (OH)_4]\ (aq) + 3H_2\ (g)$$

Inhibition Effect: Figure 2 shows the weight loss (g/cm^2) with exposure time plots for 0.3 M NaOH solution in presence and absence of inhibitors. Weight loss was found maximum in blank NaOH solution. The presence of thioureas and its derivatives as inhibitor had decreased the corrosion. Similarly figures 3-5 show the plots between weight loss and exposure period for 0.4 M, 0.6 M and 1.0 M NaOH solutions respectively in presence and absence of inhibitors. The graphs again showed the similar pattern that the weight loss is higher in blank NaOH solution and it was significantly lowered down in presence of inhibitors. Many investigations have been carried out regarding the mechanism of corrosion protection through adsorption. Compounds containing nitrogen, sulfur or oxygen atoms get adsorbed at surface of metal through coordinate bonding and protect the metal from corrosion attack. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are potential corrosion inhibitors[3]. The availability of lone pair electrons in the inhibitor molecules facilitates the electron transfer from the inhibitor to the metal, forming a coordinate covalent bond[11]. The corrosion inhibitor acts as a protective film. The strength of the adsorption bond depends on the electron density, on the donor atom of the functional group and also on the polarisability of the group. The organic substances belonging to this group contain mainly oxygen, sulfur, nitrogen atoms, and multiple bonds in the molecules that facilitate the adsorption on the metal surface[12].

Molecular Structure of Thiourea and its Derivatives:



Thiourea (TU) Phenyl Thiourea (PTU) 4-Carboxy Phenyl Thiourea (CPTU)

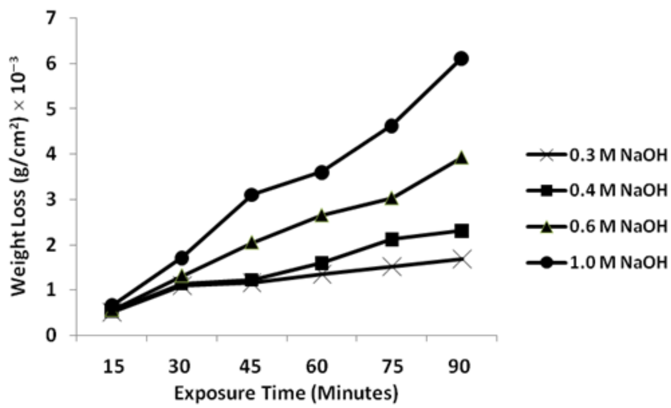


Fig. 1: Weight loss versus time plot for the dissolution of aluminum in NaOH of various concentrations

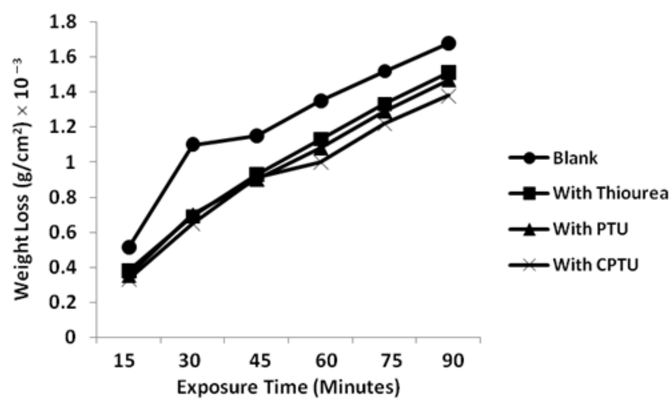


Fig. 2: Weight loss versus time plots for the corrosion of aluminum in 0.3 M NaOH in absence and presence of inhibitors.

Inhibition Efficiency: Percent inhibition efficiencies of inhibitors for dissolution of aluminum in NaOH solution of various concentrations are given in table-1 and figure 6 shows the bar chart of percent inhibition efficiency of inhibitors. The maximum efficiency was observed for carboxy phenyl thioureas (CPTU) derivative in 0.3 M NaOH solution. The percent inhibition efficiency decreased with increasing the NaOH concentration for all the inhibitors under investigation.

Conclusions: Corrosion rate of aluminum increased with increasing the concentration of NaOH solution. The % inhibition efficiency of carboxy phenyl thiourea (CPTU) was found to be the maximum in 0.3M NaOH solution.

Percent inhibition efficiency of inhibitors in 0.3M NaOH solution followed the order CPTU > PTU > TU. In 0.4, 0.6 and 1.0 M NaOH solution the percent inhibition efficiency followed the order PTU > CPTU > TU

The inhibition efficiency decreased with increasing the NaOH concentration.

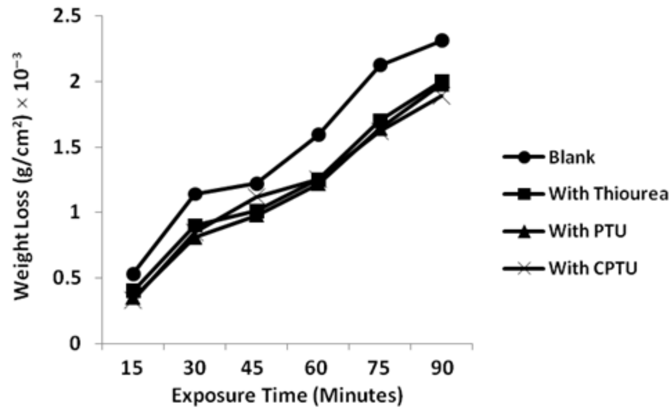


Fig. 3: Weight loss versus time plots for the corrosion of aluminum in 0.4 M NaOH in absence and presence of inhibitors.

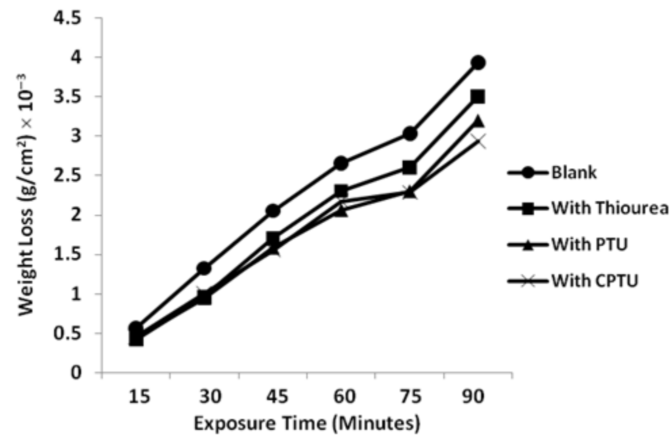


Fig. 4: Weight loss versus time plots for the corrosion of aluminum in 0.6 M NaOH in absence and presence of inhibitors.

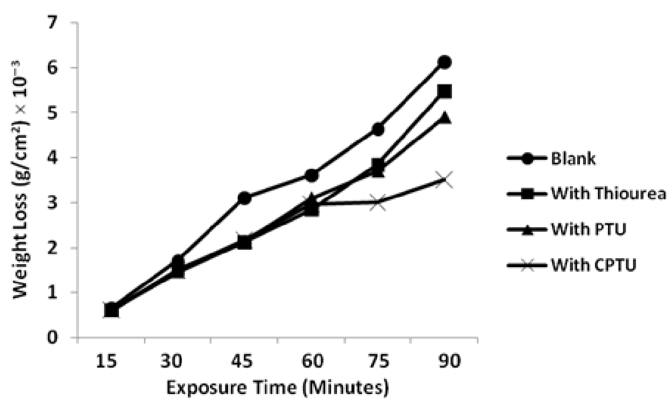


Fig. 5: Weight loss versus time plots for the corrosion of aluminum in M NaOH in absence and presence of inhibitors.

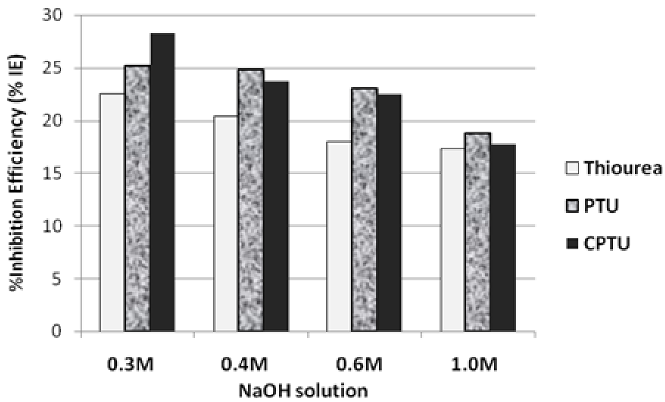


Fig. 6: Percent inhibition efficiency of inhibitors for dissolution of aluminum in sodium hydroxide solutions of various concentrations.

Table.1: Percent inhibition efficiency obtained from weight loss measurements for dissolution of aluminum in sodium hydroxide solutions of various concentrations.

Medium	% Inhibition Efficiency
0.3M NaOH + Thiourea	22.6
0.3M NaOH + PTU	25.2
0.3M NaOH + CPTU	28.3
0.4M NaOH + Thiourea	20.4
0.4M NaOH + PTU	24.8
0.4M NaOH + CPTU	23.7
0.6M NaOH + Thiourea	18.04
0.6M NaOH + PTU	23.0
0.6M NaOH + CPTU	22.5
1.0M NaOH + Thiourea	17.4
1.0M NaOH + PTU	18.8
1.0M NaOH + CPTU	17.7

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REFERENCES

1. Pourbaix, M., 1974. Atlas of electrochemical equilibria in aqueous solutions, NACE Cebelcor, Huston.
2. Davis, J.R. *et. al*, 1987. Editor, Metals Handbook, 13: 104-122 and 583-609.ninth edition, ASM International, Ohio.
3. Desai, M.N., G.H. Thanki, M.H. Gandhi, 1968. Thiourea and its derivatives as corrosion inhibitors, Anti-Corrosion Methods and MaterialsYear, 15(7): 12-16.
4. Vasanthi, B.J., L. Ravikumar, A. Selvaraj, 2008. Corrosion control of phenylthiourea polymers on aluminium in alkaline medium, Materials and Corrosion, 59(1): 14-20.
5. Quraishi, M.A., M.A.W. Khan, M. Ajmal, 1996. Anti-Corros. Methods Mater, 43, 5.
6. Murlidharan, S., S.V. Iyer, 1997. Anti-Corros. Methods Mater, 44: 100.
7. Al-Andis, N., E. Khamis, A. Al-Mayouf, H. Aboul Enicm, 1995. Corros. Prev. Control, 42: 13.
8. Hammouti, B., A. Aouniti, M. Taleb, M. Brighli, S. Kertit, 1995. Corrosion, 51: 441.
9. Prabhu, R.A., T.V. Venkatesha and A.V. Shanbhag, 2009. J. Iran. Chem. Soc., 6(2): 353-363.
10. Abdallah, M., 2004. Corros. Sci., 46.
11. Chauhan, L.R. and G. Gunasekaran, 2007. Corrosion inhibition of mild steel by plant extract in dilute HCl medium, Corros. Sci., 49: 1143-1161.
12. Quraishi, M.A., M.A.W. Khan, M. Ajmal, 1996. Influence of some thiazole derivatives on the corrosion of mild steel in hydrochloric acid, Anti-Corros. Methods Mater, 43: 5-8.