



TO STUDY THE INHIBITION EFFICIENCY OF THE CHELATING AGENTS AND THEIR METAL COMPLEXES

Bhagat.T.M.

P. G. Department of Chemistry, G.S.Gawande College, Umarkhed, Dist-Yavatmal (M.S.)

ABSTRACT

The steel binding wire was used to study the corrosion. The wire was washed with distilled water and dried by using ordinary filter paper. The wire was cut into pieces having about four inch length. The weight of each piece of wire was determined by using analytical balance. The seven beakers were arranged having labels 1 to 7. In each beaker 50 ml of 0.1 N HNO₃ were added by using burette. The chelating agent and metal complexes were added in different beaker differently while in seventh beaker only 50 ml 0.1 N, nitric acid and this beaker is termed as control. In each beaker previously weighed binding wire were dipped for 24 hours. After 24 hours, these pieces of binding wire were removed and their weights were determined after washing and drying by using analytical balance. Experiments were conducted twice and average values are used for calculation.

Keywords: Chelat, Analytical, polarization

Introduction

Inhibitors are chemicals that react with a metallic surface and protect the surface to the certain level from corrosion. Inhibitors are adsorbed on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitor, slow corrosion processes by either, increasing the anodic or cathodic polarization behavior or reducing the movement of diffusion to the metallic surface. Generally inhibitors have been classified in the following group according to its functionality.

- i) Passivating inhibitors
- ii) Cathodic inhibitors

- iii) Organic inhibitors
- iv) Precipitation inhibitors
- v) Volatile corrosion

Certain references indicates that the organic compound containing primary secondary, tertiary amines and also compound containing basic nitrogen in hetero cyclic ring exhibit inhibition tendency of metal corrosion.

The inhibitors may be forming a layer on the surface of metal by adsorption. The adsorbed layer of inhibitor produces thin layer between the metal and corroding environment which retards further corrosion. Various aromatic amines, substituted amines thio compounds, amino phenols have an inhibition tendency of metal.

Corrosion can be controlled by different ways. Chemical substances which controlled the corrosion are called as inhibitor. Most of the inhibitor compounds, forms donar-acceptor surface complex between free or π -electron of inhibitor and vacant d-orbital of metal¹⁻⁴. Nitrogen compounds have been studied as inhibitors by several workers⁵⁻⁷. It has shown that organic compounds containing hetero atom with high electron density such as nitrogen, sulphur and oxygen or multiple bond containing compounds are effective acid inhibitors⁸. It has been reported that corrosion reaction becomes much complicated in the presence of inhibitory organic molecules on metal surface⁹⁻¹¹. A metal surface in contact with sea water and organic nutrients develop passive surface films¹².

Various aromatic amines¹³, chloro substituted anilines¹⁴ and thio compounds¹⁵ in nitric acid media are also reported to be used as corrosion inhibitors. Mitra¹⁶ reported corrosion inhibition of dicyanamide. It has been shown that the inhibition takes place through strong adsorption of the molecule over metal surface.

The protective action of benzothiazole has been attributed to the formation of polymeric film of metal –BTA on the metal surface¹⁷⁻¹⁹.

Inhibitor Efficiency:

Corrosion inhibitors are chemical substances, when they are added in a small amount to an environment, then decreases the corrosion rate. The efficiency of that inhibitor is thus expressed as-

$$I. E (\%) = \frac{W_u - W_i}{W_u} \times 100$$

Where

I. E. = Inhibitor efficiency

W_u = weight loss of metal in uninhibited system.

W_i = weight loss of metal in inhibited system.

In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration e.g. a typically good inhibitor would give 95 % inhibition at a concentration of 0.008 % and 90% at a concentration of 0.004 %

Experiment

To study the inhibition efficiency of the chelating agent and their metal complexes dipping method is used. In this method, the metal wire i.e. steel wire was dipped in 50 ml 0.1 N nitric acid, chelating agent and metal complexes solution. For 24 hours.

0.1 N, HNO_3 were prepared by dissolving concentrated nitric acid (A.R. grade) in distilled water. The normality of prepared HNO_3 was determined by titrating with standard NaOH solution. This HNO_3 solution is used as a stock solution.

The metal wire

The steel binding wire was used to study the corrosion. The diameter of wire was 0.4 mm which is measure by using screw gauge. This wire is cleaned by emery paper. After cleaning, the wire was washed with distilled water and dried by using ordinary filter paper. The wire was cut into pieces having about four inch length. The weight of each piece of wire was determined by using analytical balance.

The seven beakers were arranged having labels 1 to 7. In each beaker 50 ml of 0.1 N HNO_3 were added by using burette. In first

beaker 0.1 gm 4-bromo-2-hydrazino-6-methyl benzothiazole, in second beaker, 0.1 gm of bis-4-bromo-2-hydrazino-6-methyl benzothiazole iron (II) chloride complex, in third beaker 0.1 gm, bis-4-bromo-2-hydrazino-6-methyl benzothiazole Cobalt (II) chloride complex, in fourth baker 0.1gm, bis-4-bromo-2-hydrazino-6-methyl benzothiazole Nickel (II) chloride complex, in fifth beaker 4-bromo -6-ethoxy -2-hydrazino benzothiazole (chelating agent), in sixth beaker 0.1 gm of 4-bromo-6-ethoxy-2-hydrazino benzothiazole Copper (II) chloride complex were added while in seventh beaker only 50 ml 0.1 N, nitric acid and this beaker is termed as control.

In each beaker previously weighed binding wire were dipped for 24 hours. After 24 hours, these pieces of binding wire were removed and their weights were determined after washing and drying by using analytical balance. Experiments were conducted twice and average values are used for calculation.

The initial weight and the weight of binding wire after keeping it in 0.1 N HNO_3 along with chelating agent and metal complexes were determined and recorded in table. The percentage loss and calculated inhibitor efficiency also recorded in the table No. 1.

Result and discussion:

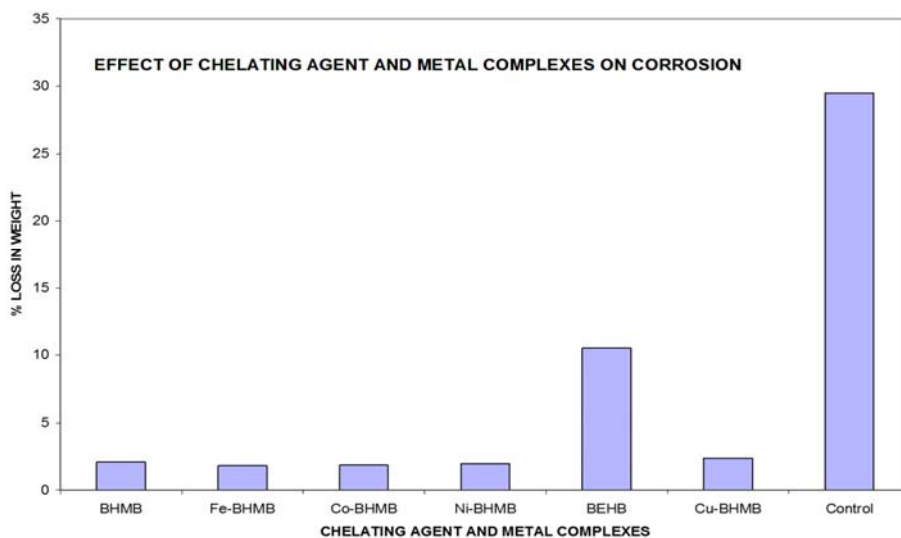
Result indicates that, 30% loss in weight is observed in 0.1N nitric acid which is maximum and it is used as control. The loss in weight of binding wire in 0.1N nitric acid is more than other six experiments carried out in presence of different chelating agent and metal complexes. It indicates that chelating agent as well as four metal complexes are not same, but it is different for different chelating agent as well as different metal complexes under study.

Inhibition efficiency results indicate that 4-bromo-6-ethoxy-2-hydrazino benzothiazole (chelating agent) have less inhibition efficiency as compared to 4-bromo-2-hydrazino-6-methyl benzothiazole (chelating agent) and metal complexes. The less inhibition efficiency may be due to presence of $-OC_2H_5$ group in chelating agent. The chelating agent 4-bromo-6-ethoxy-2-hydrazino benzothiazole has a free amino group which may decrease the oxidizing power of nitric acid. The chelating agent 4-bromo-6-ethoxy-2-hydrazino benzothiazole also contains $-OC_2H_5$ as a substituent on

benzene ring. As the $-OC_2H_5$ group is electron withdrawing group which decreases the basic character of $-NH_2$ group. Therefore the inhibition efficiency of 4-bromo-6-ethoxy-2-hydrazino benzothiazole is less than 4-bromo-2-hydrazino-6-methyl benzothiazole.

Table: 1 Effect of chelating agent and its complexes on corrosion

Sr. No	Compound	Initial weight (w_1) in gm	After 24 Hrs weight (w_2) in gm	Difference in weight (w_2-w_1) in gm	% Loss in weight	Inhibitor efficiency (IE)
1.	4-Bromo-2-hydrazino-6-methyl benzothiazole	0.4962	0.4859	0.0103	2.0757	93.13
2.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole iron (II) Chloride	0.4936	0.4846	0.0090	1.8233	94.00
3.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole Cobalt (II) Chloride	0.5347	0.5248	0.0099	1.8515	93.40
4.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole Nickel (II) Chloride	0.4879	0.4782	0.0097	1.9881	93.50
5.	4-Bromo-6-ethoxy-2-hydrazino benzothiazole	0.4896	0.4382	0.0514	10.498	65.83
6.	4-Bromo-6-ethoxy-2-hydrazino benzothiazole Copper (II) Chloride	0.5218	0.5094	0.0124	2.3763	91.73
7.	Control	0.5089	0.3562	0.1527	30	--



Its complex with Cu^{++} (4-bromo-6-ethoxy-2-hydrazino benzothiazole Copper (II) chloride complex) increases inhibitor efficiency. The inhibitor efficiency of copper

complex is found to be 91.73. This increase in inhibitor efficiency may be due to adsorption of copper metal complexes on the surface of iron wire.

Inhibition efficiency of 4-bromo-2-hydrazino-6-methyl benzothiazole and its complexes with transition metal have interesting observation. The percentage loss in 4-bromo-2-hydrazino-6-methyl benzothiazole is 2.0757% and its inhibitor efficiency is 93.13. It is observed that, inhibitor efficiency of chelating agent 4-bromo-2-hydrazino-6-methyl benzothiazole is more than the chelating agent 4-bromo-6-ethoxy-2-hydrazino benzothiazole. The reason may be presence of more basic –NH₂ group of 4-bromo-2-hydrazino-6-methyl benzothiazole as compare to –NH₂ group present in 4-bromo-6-ethoxy-2-hydrazino benzothiazole chelating agent. The observed finding indicates that 4-bromo-2-hydrazino-6-methyl benzothiazole have a more inhibitor efficiency than the metal complexes and other chelating agent 4-bromo-6-ethoxy-2-hydrazino benzothiazole. 4-Bromo-2-hydrazino-6-methyl benzothiazole retards the rate of oxidizing tendency of nitric acid.

The three complexes of 4-bromo-2-hydrazino-6-methyl benzothiazole like bis-4-bromo-2-hydrazino-6-methyl benzothiazole Iron (II) chloride complex, bis-4-bromo-2-hydrazino-6-methyl benzothiazole Cobalt (II) chloride complex and bis-4-bromo-2-hydrazino-6-methyl benzothiazole Nickel (II) chloride complex were used to study the inhibition efficiency. The result indicates that the inhibition efficiency of these complexes increases. The percentage loss in case of [Fe(BHMB)₂Cl₂].2H₂O is 2.44, the percentage loss in [Co(BHMB)₂Cl₂].2H₂O is 3.77, percentage loss in weight in [Ni(BHMB)₂Cl₂].2H₂O is 2.08 and the inhibitor efficiency of these complexes is 94%, 93.5%, 93.4% respectively. The increases in inhibitor efficiency as compare to chelating agent may be due to adsorption of metal complex on surface of steel binding wire. Not only the adsorption of metal complexes on steel wire is responsible to increase the inhibitor efficiency but also the metal complexes may reduce the oxidizing power of nitric acid. The nitric acid which is under study may be used to decompose the metal complex and decreases the concentration of nitric acid.

After decomposition of the metal complex, the chelating agent is released. The

released chelating agent decreases the oxidizing power of the nitric acid.

After decomposition of the metal complexes, the metal ions Fe⁺⁺, Co⁺⁺, Ni⁺⁺ and Cu⁺⁺ are released and they move freely in the solution. Further metal ions may gather on metal wire forming a single cell (Nernst potential equation) which may causes loss of oxidation of steel wire

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