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# High molecular weight heterocyclic aminothiazole adduct for protection of carbon steel in both 3.5% NaCl and 0.8 M HCl mediums

Heba A.Mohamed Department of Polymers and Pigments, National Research Center, (EGYPT) E-mail : hebaamohamed@gmail.com

# ABSTRACT

In recent years, there is a considerable effort devoted to find novel and efficient corrosion inhibitors. High molecular weight heterocyclic aminothiazole adduct (ATS) is prepared through epoxy ring opening reaction of epoxidized soybean oil (EPS) with 2-aminothiazole (AT) at 120 °C for 3 hours. The reaction product is characterized physically and is evaluated with infrared spectroscopy (IR) and gel permeation chromatography (GPC). The prepared ATS is investigated as corrosion inhibitor for carbon steel in both 0.8 M HCl and 3.5% NaCl mediums. Weight loss, scan electron microscope (SEM) and corrosion tests are different used techniques to prove the efficiency of ATS to protect carbon steel from corrosion. Effect of the type of exposure mediums of carbon steel on the efficiency of ATS is studied. It is found that high molecular weight heterocyclic ATS can protect carbon steel from corrosion. The corrosion inhibition efficiency of ATS increases by increasing its concentration in both 0.8M HCl and 3.5% NaCl mediums. ATS shows high corrosion inhibition in 3.5% NaCl medium and moderate corrosion inhibition in 0.8 M HCl due to protonation of ATS at low PH medium and the protonated ATS, becomes weakly adsorbed on the carbon © 2014 Trade Science Inc. - INDIA steel surface.

#### INTRODUCTION

Among several methods used in combating corrosion problems, the use of organic compounds containing nitrogen, sulphur and oxygen atoms remains the most effective method, where corrosion poses serious problem to the service lifetime of alloys used in industry<sup>[1-7]</sup>.

Heterocyclic compounds with essential amino or mercapto group give better corrosion inhibition for metals compared with linear amino or mercapto compounds. The planarity of the heterocyclic compounds in addition to the lone pair of electrons present on het-

# KEYWORDS

Heterocyclic corrosion inhibitor; Adsorption; Acidic medium; Scan electron microscope; Weight loss; Carbon steel.

eroatoms provide extra coverage and adsorption of these structures on the metal surface<sup>[8-16]</sup>.

The adsorption of organic molecules at the metal/ solution interface is of great interest in surface science. Since the degree of protection of metals is a function of adsorption, the investigation of the relation between corrosion inhibition and adsorption is of great importance<sup>[17,18]</sup>.

The existing data show that most organic inhibitors act by adsorption on the metal surface. Their efficiency as a successful inhibitor is mainly dependent on their ability to get adsorbed on the metal surface which con-

#### RRPL, 5(2) 2014

# Full Paper 🛥

sists of the replacement of water molecules at a corroding interface<sup>[19,20]</sup>

Low molecular weight aminothiazole (AT) and its derivatives are reported to have anti corrosive properties<sup>[21]</sup>. In addition aminthiazole and its derivatives are healthy compounds and play an important role in biological reactions because of their antimicrobial<sup>[22]</sup>

It is mentioned that high molecular weight amines and heterocyclic thiazoles with repeating active units and with high elcetron density have better adsorption and better corrosion inhibition efficiency than low molecular weight corresponding organic compounds as corrosion inhibitor and as metal coverage in addition to its novelty<sup>[8,23,24]</sup>.

In this research a novel high molecular weight heterocyclic heterocyclic aminothiazole adduct (ATS) is prepared and confirmed by infra- red (IR) and Gel permeation chromatography (GPC). It is evaluated as corrosion inhibitor in 3.5% NaCl and 0.8M HCl for uncoated carbon steel by weight loss and scan electron microscope techniques.

### MATERIALS

Aminothiazole, chemical structure  $C_3H_4N_2S$ , MW 100.14, melting point 86-89°C is delivered from Sigma-Aldrich, USA. Epoxidized soybean oil, Oxirane content 6.5% is delivered from Hobum Company, Germany. Polyethylene glycol sorbitan monolaurate is delivered from Sigma Aldrich under the trade name Tween20, HLB 16.7. Sorbitane monolurate is delivered from Sigma Aldrich under the trade name Span20, HLB 8.6. The used carbon steel alloy composition is 0.08% C, 0.35% Mn, 0.014% P, 0.018% S, 0.17% Si and the rest is Fe.

#### **EXPERIMENTAL**

Preparation of ATS is confirmed by FTIR spectrometer, Nexus 670, Nicolt, USA, (Resolution 4cm<sup>-1</sup>), according to ATSM D 5670-95, Micro Analytical Center, National Research Center, Egypt.

ATS molecular weights is determined by gel permeation chromatography (GPC)<sup>[25]</sup> using Agilent-1100 GPC-Agilent technologies- Germany. THF was used as the eluent with flow rate 1ml min<sup>-1</sup>. Commercially

Research & Reviews On Polymer available linear poly methyl methacrylate and polystyrene standards were used to calibrate the columns. The GPC apparatus was run under the following conditions: Flow rate = 2.000 ml/min, Injection volume = 100.000 µl, Sample concentration = 1.000 g/l. The refractive index detector was G-1362A with 100-104-105 Ao AltrATSyragel columns connected in series.

Carbon steel panels must be treated<sup>[26]</sup> before use by removing all detrimental foreign matter such as oil, grease, dirt, and other contaminants by acetone, removing of all rust with different grades of emery paper, rubbing the panels with a clean cloth to remove any residual impurities and coated immediately.

ATS is dispersed in water through emulsification process with co- emulsifier span 20 and non-ionic emulsifier tween 20, using high speed homogenizer. 0.25 g ATS is dissolved in 0.2 g span 20, then added to 0.5% Tween 20 during high speed stirring and complete stirring for 30 minutes.

A series of concentrations (0.05, 0.10, 0.15, 0.20, 0.25) of ATS is prepared in acidic medium by dissolving ATS in 0.8 M HCl. In NaCl medium, ATS should first emulsified as described above to be dispersed in water.

Weight loss measurements are done according to ATSM D 2688-94 (1999) For 2weeks in both 0.8M HCl and 3.5 NaCl for uncoated carbon steel panels The obtained results are calculated for only one face of the steel panels.

Surface morphology of some chosen uncoated carbon steel specimens are examined in both 3.5% NaCl and 0.8M HCl in the absence and presence of 0.25% ATS, using scanning electron microscope (JXA – 840 A, JEOL - Japan).

## **RESULTS AND DISSCUSION**

# Preparation and characterization of heterocyclic amine adduct (ATS)

High molecular weight heterocyclic aminothiazole adduct (ATS) is prepared through epoxy ring opening reaction of epoxidized soybean oil (EPS) with 2-aminothiazole (AT) at 120 °C for 3 hours in sealed glass tube. The prepared adduct is freely soluble in benzene, toluene, xylene, acetone and butyl acetate. This means that no cross-linking has occurred during the reaction.



43

The reactions were carried out according to the chemical equation, Figure 1.



Figure 1 : Chemical reaction of ATS, n= no. of oxirane per EPS molecule

# Infra-red spectroscopy

As shown in Figures 2 (a), (b) & (c) the preparation of ATS is followed up by infra-red spectroscopy (IR).

Figure 2 (a) corresponding to epoxidized soybean oil (EPS) shows a very characteristic band of epoxy group at 825 cm<sup>-1</sup>. The ester group exhibited two bands, a strong band at 1735 cm<sup>-1</sup> due to (C=O) group and a broad band at 1160 cm<sup>-1</sup> due to (C=O) group. Also, there was a strong band near 2900 cm<sup>-1</sup> due to (C-H) attached to the ester group. With respect to Figure 2 (b) of AT, primary amine bands appears at 3300 - 3500 cm<sup>-1</sup> (two bands) and a bending band at 1560- 1640 due to primary (N-H) group. According to Figure 2 (c) the IR spectra of the ATS confirms that all epoxy groups of the EPS are consumed during the reaction with the primary amine AT, where the bands of the epoxy group 825 cm<sup>-1</sup> are completely diminished. Moreover, new characteristic bands of secondary amino groups (one band) and hydroxyl groups appears (they appears as an overlapped broad peak) at 3200–3500 cm<sup>-1</sup>. Also another bending band appears near 1500 cm<sup>-1</sup> due to secondary aminogroup and another band due to C-N appears at 1000-1350 cm<sup>-1</sup>.

#### Molecular weight measurements

Gel permeation chromatography technique is used to determine weight-average molecular weight ( $\overline{M}_W$ ), number average molecular weight ( $\overline{M}_n$ ) and polydispersity (D =  $\overline{M}_W/\overline{M}_n$ ) of EPS and ATS. The obtained results are summarized in TABLE 1.

According to TABLE 1, it is clear that GPC M.wt of EPS and ATS adduct are approximately equivalent to the theoretical molecular weight. This proves that the reaction between epoxidized soybean oil (EPS) and heterocyclic ATS are completely finished without any by-products.





Wavenumber (cm-1)

Figure 2: IR chart of: (a) Epoxydized soybean oil, EPS (b) Aminothiazol, AT (c) Aminothiazol-soybean oil adduct, ATS

TABLE 1 : Molecular weight measurements of EPS and ATSby gel permeation chromatography

Sample	Theoretical M.wt, (g/mol)	₩w, (g/mol)	Mn, (g/mol)	D
Ep-So	1000	1226.30	845.35	1.451
ATS	1400	1396.50	423.21	3.2901

### Performance of ATS as corrosion inhibitor

Performance of ATS as corrosion inhibitor in both 3.5% NaCl and 0.8 M HCl is studied by weight loss determination of the uncoated immersed samples of carbon steel and by scan electron microscope technique. Inhibition efficiency of the investigated ATS is determined according to equation 1.

$$I(\%) = 100 X (Wo - Wi) / Wo$$
 (1)

Where, Wo and Wi are the weight loss values in absence and in presence of the prepared ATS, respectively.

### (a) Evaluation of ATS in 3.5% NaCl

In order to make ATS dispersed in aqueous medium, a series of different concentrations of ATS (0.05, 0.10, 0.15, 0.20, 0.25 g) are firstly emulsified by dissolving ATS in 0.2 g of span20 and then adding ATS/ span20 to a continuous phase of 100 ml of 0.5% Tween20 during stirring with high speed homogenizer with minimum 4000 round per minute.

Weight loss determination of the immersed uncoated carbon steel in 3.5% NaCl is plotted in Figure 3. The related corrosion inhibition efficiency of ATS is calculated according to equation 2 and plotted in Figure 4.

Both Figures 3 and 4 declare that, corrosion inhibition efficiency of ATS icreases by increasing its concentration and reaches up to 90.17% at 0.25% ATS (in the emulsified form.

The morphology of the immersed carbon steel in 3.5% NaCL is investigated by SEM technique in ab-

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sence and presence of 0.25% ATS and represented in Figures 5 a & b.

Smoothening of carbon steel surface in presence of 0.25% ATS is observed in Figure 5b compared with high degree of roughness in absence of ATS in Figure 5a. Surface smoothening is caused by the adsorption of ATS on the steel surface and thus, the surface is fully covered and protected

#### (b) Evaluation of ATS in acidic medium (0.8M HCl)

Different concentrations of ATS (0.05, 0.1, 0.15, 0.2, 0.25 g) are weighted and dissolved in 100 ml of 0.8M HCl in addition to 0.8M HCl free from ATS (acidic blank). Performance of ATS as corrosion inhibitor for carbon steel samples in 0.8 M HCl is investigated by weight loss technique. In addition surface morphology of immersed carbon steel in 0.25 g ATS/



Figure 3 : Weight loss determination of the immersed carbon steel in 3.5% NaCl



ATS Concentration in NaCl medium % Figure 4 : Corrosion inhibition efficiency of ATS in 3.5% NaCl medium







0.8M HCl is investigated by scan electron microscope.

Weight loss of immersed carbon steel panels in 0.8M HCl, 0.05g ATS/ 0.8M HCl, 0.1g ATS/ 0.8M HCl, 0.15g ATS/ 0.8M HCl, 0.2g ATS/ 0.8M HCl and 0.25g ATS/ 0.8M HCl, are determined and calculated for two weeks at room temperature. The obtained results are plotted in Figure 6.

Corrosion inhibition efficiency of ATS is calculated according equation 2 and represented graphically in Figure 7

It is clear that ATS can inhibit corrosion moderately and its efficiency increased by increasing its concentration up to 50.47% for 0.25% ATS/ 0.8M HCl for two weeks.

Figures 8 (a&b) show the micrographs for uncoated immersed carbon steel in 0.8M HCl in absence and 0.25g. It is clear that surface morphology of carbon steel is harmly affected and completely covered with rust in the absence of ATS, which causes high degree of roughness. On the other side, in the presence of 0.25% ATS, the steel surface is moderately affected with rust and aproximately 50% of the steel surface is exposed to roughness and pits.

The moderate inhibition efficiency of ATS in 0.8M

HCl (IE %) may be due to the protonation of ATS in acidic medium, thus it becomes cation existing in equilibrium with the corresponding molecular form as shown in Figure 9.

According to the schematic diagram of the adsorption mechanism of Figure 9, the protonated ATS, becomes weakly adsorbed on the carbon steel surface, which is positively charged in acidic medium<sup>[27,28]</sup>. Thus it becomes cation existing in equilibrium with the corresponding molecular form.

The S atom of the thiazole ring is expected to have weak coordination ability<sup>[27,28]</sup>, since the lone pair on this atom participates in the resonating structure of the molecule, resulting in a reduction of electron density on the S atom and a decrease in the electron donating power.

The O atom in the hydroxyl group of high molecular weight ATS gives the adduct extra advantage compared with low molecular weight aminothiazole (AT). It is clear that AT has only three lone pairs of electrons which reduced to two lone pairs of electrons in low pH mediums. The ATS molecule has four repeated heterocyclic ring and four atoms with four lone pairs of electron available for coordination, which are N, S atoms

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in the heterocyclic ring, O atom in the hydroxyl group and the N atom of amino group. Each four lone pairs of electrons are reduced to three in case of ATS in low pH medium

#### CONCLUSIONS

The prepared aminothiazole adduct structure is confirmed by IR and its molecular weight is proved by GPC. The reaction product was relatively high molecular weight adduct and had both primary amino group and hydroxyl groups with available lone pairs of electrons in addition to the planarity of the heterocyclic structure which was rich with nitrogen and sulfur atoms with high electron density.

The ATS under investigation has high corrosion inhibition efficiency in 3.5% NaCl which increases with increasing its concentration (IE 90.17% for 0.25% ATS).

ATS has moderate inhibition efficiency in 0.8M HCl (IE 50.47%), since the molecule is protonated in acidic medium. So the protonated ATS, becomes weakly adsorbed on the carbon steel surface, which is positively charged in acidic medium<sup>[27,28]</sup>.

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