

SYNTHESIS AND USES OF INHIBITOR 6-SUBSTITUTED-2-AMINOBENZOTHAZOLES FOR MILD STEEL

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Abstract: Aminobenzothiazole and its derivatives have been synthesised and used as inhibitors for corrosion of mild steel. The mild steel sheet used for the investigation the following composition C 0.14, Mn 0.35, Si 0.17, S 0.025, P 0.03 and rest Fe. Weight -loss method, Potentiostatic Polarisation Technique, AC Impedance Technique, Hydrogen Permeation Technique, Scanning Electron Microscopy and Auger Electron Microscopy were used for Characterization.

Keywords: Arylthiourea, 6-substituted-2-aminobenzothiazoles, Inhibitors, Corrosion

Introduction

Heterocyclic compounds comprise a potential class of corrosion inhibitors. There is a wide consideration in the literature regarding corrosion inhibition studies by nitrogen containing heterocyclics [1-3]. On the contrary, investigations on heterocyclics bearing N and S atoms in t ring have received a little attention. 2-mercaptobenzothiazole has been reported as an effective corrosion inhibitor the same for copper and its alloys in different corrosive environments [4-5]. Singh and co-workers have studied the effect and 2-mercaptobenzothiazole on corrosion inhibition and hydrogen absorption in acid medium [6-7]. A few hydrazinobenzothiazoles were synthesised and evaluated as acid corrosion inhibitors. Survey of literature reveals that 2-aminobenzothiazole and its 6-substituted analogues have not been studied as acid corrosion inhibitors.

This study deals with the influence of 2-aminobenzothiazole and its derivatives on corrosion of mild-steel in 1N HCl and 1N H₂SO₄. The weight loss measurements were conducted in both the acids at different temperatures (40-60°C) using 100-500 ppm concentrations for all the inhibitors. Polarization experiments have been performed at (35 ± 2°C) to understand the behaviour of these compounds as corrosion inhibitors. Hydrogen permeation experiments were also carried out to study the effect of these compounds on the permeation of hydrogen through the steel surface. Elemental analysis by Auger Electron Spectroscopy (AES) has been carried out.

Materials Required

Test Specimen

The mild steel sheet used for the investigation had the following composition:

C	Mn	Si	S	P	Fe
0.14	0.35	0.17	0.025	0.03	rest

Test Solution

A.R. grade sulphuric and hydrochloric acids were used. Double distilled water was used to prepare all the solutions required for the experiments. 1-2% Ethanol was used to dissolve inhibitors.

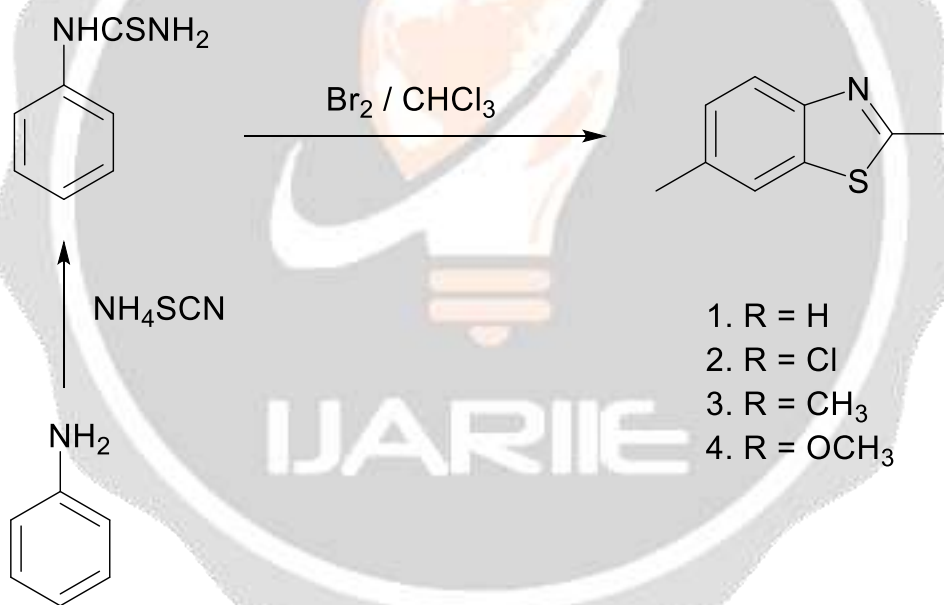
Inhibitors Used

1. 2-aminobenzothiazole (ABT)
2. 2-amino-6-chlorobenzothiazole (ACLBT)
3. 2-amino-6-methoxybenzothiazole (AMEOBT)
4. 2-amino-6-methylbenzothiazole (AMEBT)

Synthesis of Inhibitors

Synthesis of inhibitors 6-substituted-2-aminobenzothiazoles

Preparation of p-substituted arylthiourea [8,9]: An appropriate p-substituted aniline (0.1 mol) was dissolved in a mixture of concentrated HCl (9ml) and water (25 ml) by warming on a water bath. The solution of amine hydrochloride thus obtained was cooled and solid ammonium thiocyanate (0.1 mol) added. After the addition, the reaction mixture was heated on a water bath for 5 hours. Thereafter, the reaction mixture was cooled and the precipitated crude product was filtered, washed with water, dried and crystallized from aqueous ethanol. P-substituted arylthioureas, thus prepared are phenylthiourea: m.p.148 °C. P-tolylthiourea: m.p.180 °C, p-anisidylthiourea: m. P. 209 °C, p-chlorothiourea: m.p.174 °C.



Scheme-1

Preparation of 6-substituted-2-aminobenzothiazoles [10,11] (Scheme-1): To a suspension of an arylthiourea (0.1 mol) in chloroform (100 ml); bromine (0.15 mol) in chloroform (100 ml) was added. The mixture was heated under reflux for 15 minutes which was accompanied by the evolution of dense white fumes of hydrogen bromide. After the reaction was over, chloroform was distilled off and the semi-solid product, thus obtained, was treated with sulphurous acid till the brown colour was discharged and the solid dissolved. The solution was then filtered from undissolved matter ammonia. The solid which separated out was filtered, washed with water, dried and crystallized from ethanol. 2-aminobenzothiazole: m.p.128°C, 2-amino-6-chlorobenzothiazole: m.p.197 °C.

Technique Employed

The experimental work was carried out with the help of following techniques such as- Weight -loss method, Potentiostatic Polarisation Technique, AC Impedance Technique, Hydrogen Permeation Technique, Scanning Electron Microscopy and Auger Electron Microscopy for study of synergism of corrosion inhibitors for metals.

Result And Discussion

The inhibition efficiency of all aminobenzothiazoles except ACLBT decreases with rise in temperature. The compound ACLBT maintains inhibition efficiency of nearly 97% in both the acids indicating its stronger adsorption over the metal surface. The higher inhibition efficiency obtained for the chloroderivative may be attributed to high dipole moment of the molecule. Smialoska et. al. [12] have observed similar behaviour of chlorosubstituent in the case of thiophene derivatives. Recently Gad-Allah et. al. [13] have also reported that chlorosubstituted amino pyrazole gives better inhibition efficiency than parent compound during acid corrosion of copper in the presence of amino pyrazoles.

It is found that, inhibition efficiency increases with increase of inhibitor concentrations from 100 to 500 ppm. Maximum Inhibition efficiency is achieved by these compounds at a concentration of 500 ppm, further increase of concentration does not cause any appreciable change in the performance of these inhibitors. The inhibition efficiency (IE) values of Aminobenzothiazole and its derivatives in 1N HCl at 40 °C follows the order: ABT > ACLBT > AMEOBT > AMEBT.

In the case of 1N H₂SO₄, the order of corrosion inhibition caused by different compounds for a common concentration of 400 ppm is as follows: ACLBT >> ABT > AMEOBT >> AMEBT

Lesser inhibition shown by methoxy and methyl derivatives as compared to the parent and its chloroderivative may be attributed to the orientation of these groups in the ring, which may be responsible for influencing the extent of inhibition. These groups might prevent a flat orientation of molecules resulting in lesser coverage on the metal surface and lesser inhibition.

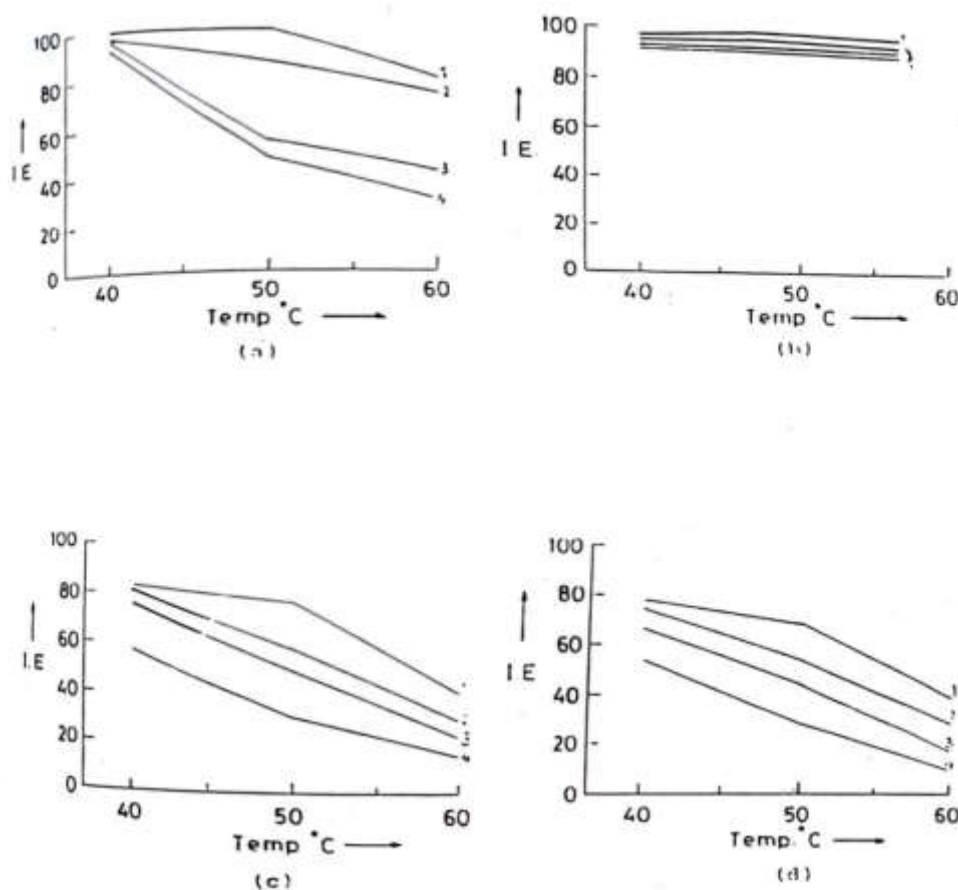


Figure 1. The variation of Inhibition Efficiencies with temperature in 1N HCl, 1, 500 ppm; 2, 400 ppm; 3, 300 ppm; 4, 200 ppm. a, ABT; b, ACLBT; c, AMEOBT; d, AMEBT.

The higher inhibition efficiency for methoxy derivative than methyl derivative can be explained in the following way. According to Pearson's classification of "HSAB" principle (Hard and Soft Acid Bases) class (a) acid prefer to bind to "hard or non-polarizable bases" and class (b) acids prefer to bind to "soft or polarizable bases". Since class (a) are themselves "soft" a simple rule is proposed. Hard acids bind strongly to hard bases and soft acids bind strongly to soft bases. In methyl derivative the inductive effect of methyl group makes the nitrogen centre a "softer base". According to this classification, ferrous ions are intermediate acids, ferric ions are hard acids. So, both these ions would prefer to form a weaker bond with a soft base, methyl compound, (AMEBT). This may lead to lesser adsorption with methyl derivative (AMEBT) and lesser inhibition of corrosion of mild steel in acids.

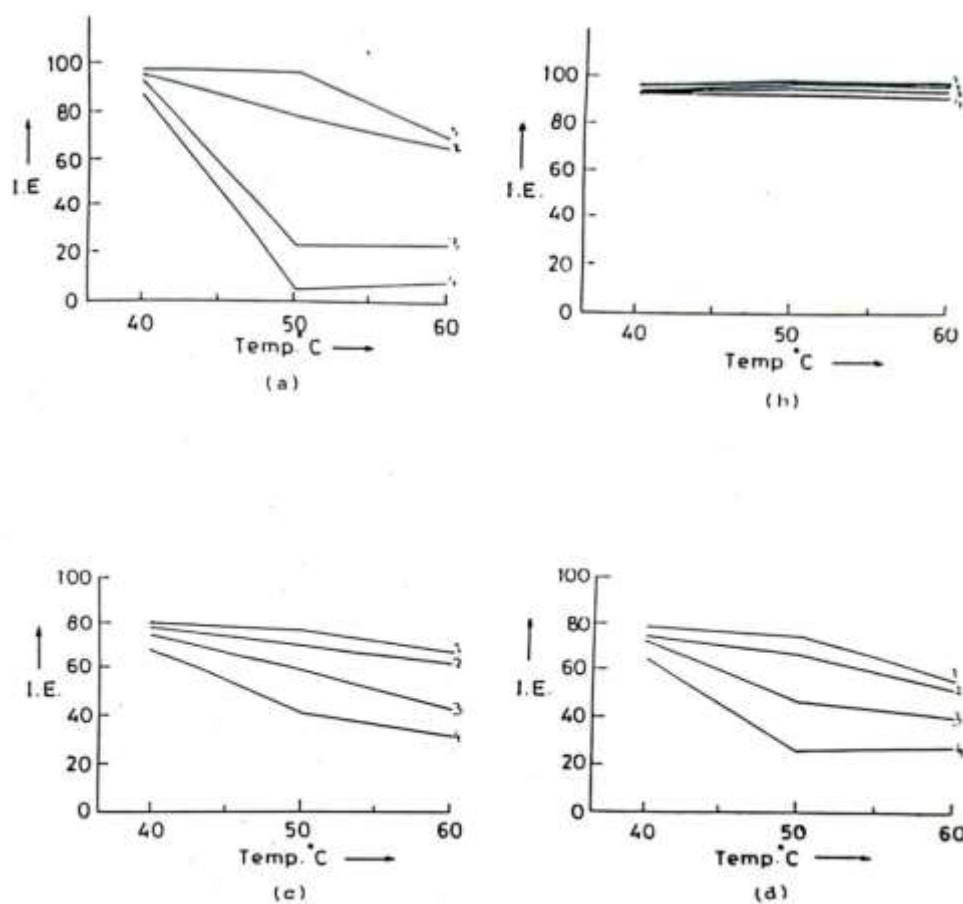


Figure 2. The variation of Inhibition Efficiencies with temperature in 1N H₂SO₄, 1, 500 ppm; 2, 400 ppm; 3, 300 ppm; 4, 200 ppm. a, ABT; b, ACLBT; c, AMEOBT; d, AMEBT.

But methoxy derivative is a harder base as compared to methyl derivative, so it forms a strong bond with ferrous and ferric ions which leads to more adsorption and more inhibition. The inhibition of corrosion by ABT and its derivatives may be due to the adsorption of inhibitor molecules on the metal surface. The adsorption of inhibitor molecules on the metal surface can be explained in terms of following interactions: (i) Lone pairs of electrons of N and S atoms of the thiazole ring and the metal surface. (ii) π -electrons of benzene and thiazole ring and the metal surface.

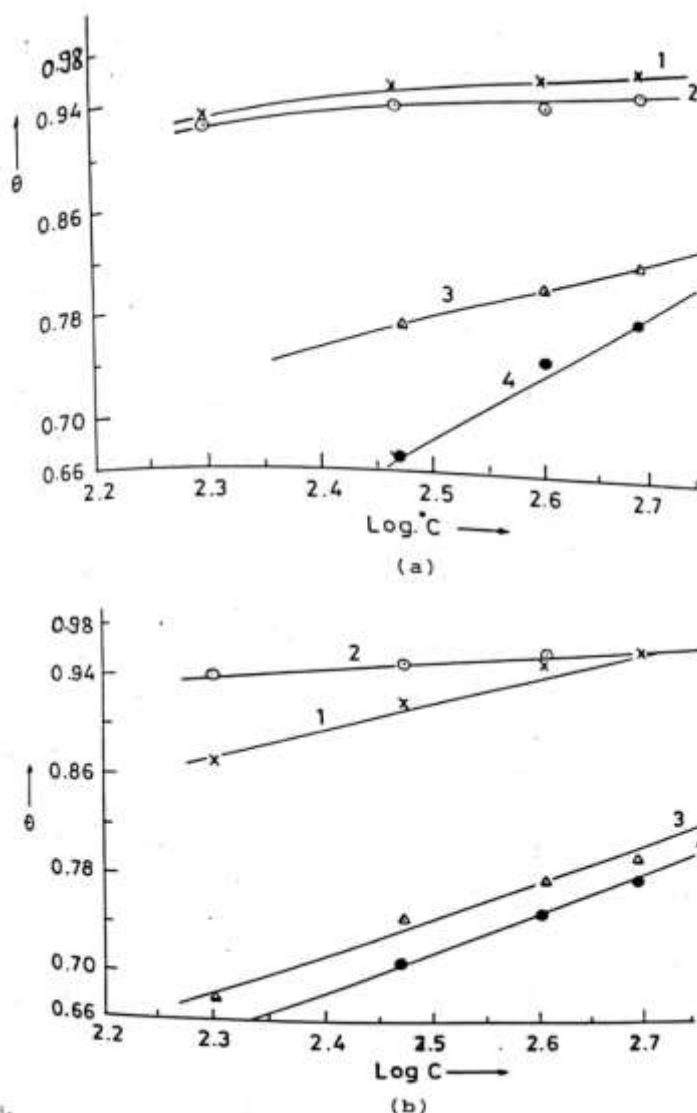


Figure 3. The Temkin Isotherm Plots from 1N HCl and 1N H₂SO₄ at 40 °C
 a, 1N HCl; b, 1N H₂SO₄. 1, ABT; 2, ACLBT; 3, AMEGBT; 4, AMEBT.

Conclusion

The main conclusions drawn from the studies are as Aminobenzothiazole and its derivatives have been found to perform well in both the acids, but a better performance is noticed in the case of HCl. In sulphuric acid, Aminobenzothiazole and chloroderivative behave predominantly as cathodic; methoxy and methyl as mixed. Whereas in hydrochloric acid methoxy and methyl derivatives behave predominantly as cathodic; parent and chloroderivative as mixed type. All the compounds reduce the hydrogen permeation current considerably in both the acids. The adsorption of compounds on the mild steel surface from both the acids obeys Temkin's adsorption isotherm. It is found from AES that the inhibitor molecules are adsorbed on the metal surface.

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