Inhibitive thiazole-tetrachlorophthalamic acid sodium salt behavior against 0.02N sulfuric acid corrosion of carbon steel

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ABSTRACT

N-(substituted) 3,4,5,6-tetrachlorophthalamic acid(1) had been prepared by the reaction of 3,4,5,6-tetrachlorophthalic anhydride with 2-amino thiazole then converted to its corresponding sodium salt (2) via addition of sodium hydroxide solution. The resulted salt (2) was subjected to weight loss study of carbon steel in 0.02 N of sulfuric acid for 24, 120, and 168 hrs. The moderated obtained results showed decreasing in corrosion rate after compound (2) addition compared with acid presence only.

KEYWORDS: corrosion, sulfuric acid, carbon steel, thiazole, tetachlorophthalic anhydride, amic acid.

INTRODUCTION

One of the most serious problems in the world especially in industry is corrosion which can be defined as the degradation of a material's properties or mass over time due to environmental effects. For most metallic materials, the natural tendency of material's compositional elements to return to their most thermodynamically stable state by formation of oxides or sulfides, or other basic metallic compounds generally considered to be ores with slow process rate.

Under normal circumstances, iron and steel corrode in the presence of both oxygen and water. The rate of corrosion is increased by the acidity or velocity of the water, by the motion of the metal, by an increase in the temperature or aeration, by the presence of certain bacteria, or by other less prevalent factors [1].

The use of inhibitors is one of the most practical methods for protecting materials against corrosion, especially in acidic media. They have been widely studied in many industries to reduce the corrosion rate of metal materials in contact with aggressive medium. Organic compounds containing nitrogen, sulfur, and oxygen atoms are well-known acid inhibitors where their efficiency depends on their abilities to be adsorbed on the metal surface with the polar groups acting as the reactive centers [2].

The various experimental techniques and theoretical methods have been improved to clarify the relation between the efficiency (by depending on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms) and physic-chemical propertiesof inhibitor molecules such as structure and functional groups, to the possible steric effects and electronic density of donor atoms [3,4].

Among them, N-heterocyclic compounds are considered to be the most effective corrosion inhibitorsand reported as good corrosion inhibitors for iron or steel in acidic media [5,6,7,8, 9,10,11,12,13].

It is accepted that N-heterocyclic compounds exert their inhibition via adsorption on the metal surface through N- heteroatom, as well as aromatic rings in their molecular structures. The adsorption of inhibitor on steel/solution interface is influenced by the chemical structures of the inhibitors, the nature and charged surface of metal, the distribution of charge over the whole inhibitor molecule and the type of aggressive media.

The size, orientation, shape and electric charge on the molecule determine the degree of adsorption and the inhibitor effectiveness [14,15,16] such as organic compounds containing sulfurfor steels in acidic media where polar organic compounds are adsorbed on the metal surface, forming a charge transfer complex bond between their polar atoms and the metal [17,18,19,20].

The aim of this paper is to study the effect of 0.02 N H_2SO_4 as a corrosive medium on carbon steel with and without presence of newly prepared and characterized thiazole-amic acid sodium salt by applying weight loss method.

MATERIAL AND METHODS
Instruments and Chemicals,
Instruments, Atomic Absorption Spectrophotometer, Shimadzu. Japan. SpectroMax$_x$, stationary metal analyser, AMETEK Spectro-Analytical Instrument (Germany, 2012/model). Melting points were determined on Gallenkamp capillary melting point apparatus. FTIR spectra were recorded using KBr discs on Shimadzu FTIR-8400 Fourier Transform Infrared spectrophotometer.

Chemicals: All the used chemicals were from Fluka and BDH and used without further purification.

Synthesis steps:
Synthesis of N - (substituted) 3, 4, 5, 6 - tetrachlorophthalamic acid (1):
This newly derivative had been synthesized according to literature [21]: A solution of (0.01mol) of amino compound (2-aminothiazole) in (25mL) of acetone was added dropwise to a solution of (0.01 mol) of cyclic anhydride (3,4,5,6 - tetrachlorophthalic anhydride) in (25mL) of acetone with stirring and cooling. Stirring was continued for four hours then the white precipitated amic acid was filtered off, washed with diethyl ether, dried, and recrystallized from cyclohexane. Yield: 84%, m.p (216-218)^{o}C. FTIR data: (O-H), (N-H):3416 cm^{-1}, (C=O) acid, amide:1696 cm^{-1}, (C=N): 1635 cm^{-1}, (C=C): 1557 cm^{-1}, (C-S): 645cm^{-1}, (C-Cl): 1050 cm^{-1}.

Synthesis of amic acid sodium salt (2) [22]: The white sodium salt was obtained by adding an alcoholic solution of the prepared amic acid was neutralized with concentrated aqueous NaOH, and the crystals that precipitated by adding a large amount of acetone were separated, dried and recrysallized from ethanol. Yield: 55%, m.p (>300)^{o}C. FTIR data: (C=O) carboxylate: 1608 cm^{-1} (asym. COO$^-$) and 1435cm^{-1} (sym. COO$^-$), (C=O) amide:1608 cm^{-1}, (N-H): 3414 cm^{-1}, (C-S): 651cm^{-1}.

Carbon steel species preparation:
The circular carbon steel sheets of 2.5 cm x 0.02 cmwere abraded with a series of emery paper (grade 320-500-800) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed at inclined position in beakers which contained 50 ml of the studied sulfuric acid concentration with different concentrations of the inhibitor.

The aggressive acid solution (with or without inhibitor presence) was open to air. After a specific time, the specimens were taken out, washed, dried, and weighed accurately.

The material composition employed for the present work was characterized with two different instrumentations (Atomic Absorption Spectrophotometer and SpectroMax$_x$/ stationary metal analyser) to specify its actual metallurgical type (in percent) and they were: C% : 0.187, Si%: 0.311, Mn%: 1.030, Fe%: 98.3.

RESULTS AND DISCUSSION
3, 4, 5, 6 - tetrachlorophthamic acid substituted with thiazole as heterocycle on nitrogen atom was synthesized via reaction of equimolar amounts of this heterocyclic amine and 3, 4, 5, 6 - tetrachlorophthalic anhydride.The conversion of the prepared tetrachlorophthalamic acid (1) to its corresponding sodium salt (2)had been done via treatment with sodium hydroxide solution (Scheme (1)).The reason for synthesis of this salt is to find out the possibility of introducing (2) (as water soluble salt) in suitable application such as corrosion inhibitors in acidic medium.

Corrosion by its simplest definition is the process of a metal returning to the material's thermodynamic state which is electrochemical reaction that follows the laws of thermodynamics and it is time and temperature dependent. Corrosion in aqueous solutions is the most common of all corrosion processes [23].

The concern for corrosion by sulfuric acid has increased in the oil and gas industry because of the burning of fuels is a major cause of global warming or the global climatestability that resulted in one way or other from the transformation of H_2S and SO_x produced during oil extraction and refining into concentrated sulfuric acid.

Carbon steel (excellent mechanical and low cost) is the most widely used as constructional material in many industries, susceptible to corrosion in environment containing oil production, and used in large tonnages in the related chemical processing, petroleum production and refining [24].

When carbon steel contacts dilute sulfuric acid, an

immediate attack on the metal takes place with the formation of hydrogen gas and ferrous ions. The rate of corrosion of carbon steels in dilute acids depends strongly on steel chemical compositions; especially the carbon content and the reasons for this unusual experimental result are not clear [25].

The durability of equipment's made of carbon steel depends on the preservation of the sulfate layer that form from carbon steel – sulfuric acid contacting and hydrogen producing and this ferrous sulfate layer prevents the metal against further attack by acid.

The corrosion rate of a metal, accompanied by the formation of a protective layer of corrosion products,is determined by one of the following stages: the diffusion of the oxidant (the sulfuric acid) to the metal surface through the corrosion product layer ($FeSO_4$ in the case of carbon steel); or the diffusion rate of the corrosion products from the metal surface toward the bulk solution. The most important factors that cause an increase in the corrosion rate are the $FeSO_4$ solubility in the acid, the temperature and the relative movement between the metal and the acid [26].

Corrosion of metallic surfaces[23] can be controlled or reduced by the addition of chemical compounds to the corrodent. This form of corrosion control is called inhibition and the compounds added are known as corrosion inhibitors, which is one of the most common effective and economic methods to protect metals especially in acid media [27].

The majority of the well-known inhibitors are organic compounds containing heteroatom, such as O, N, or S and that, at the same time, contain N and S in their structures are of particular importance, since these provide an excellent inhibition compared with the compounds that contain only N or S [28].

The circular carbon steel sheets were studied in different concentrations of the inhibitor with 0.02N of sulfuric acid.

All the aggressive acid solutions were open to air. After a specific time, the specimens were taken out, washed, dried, and weighed accurately. The weight loss of carbon sheets at the lab temperature was obtained. The corrosion rate ($mg.cm^{-2}.min.^{-1}$) was calculated from equation 1:

$$R_{corr.} = W / S .t ………… 1$$

Where,

W is the weight loss of the tested carbon steel sheets (mg),
S the total area of one carbon steel specimen (cm^2), and
t is the immersion time(min.).

The surface coverage ( ), percentage protection efficiency (inhibition efficiency) P% was calculated (equations 2 and 3):

  = [wt loss (uninh.) – wt loss (inh.)] / wt loss (uninh.) …….2

P % = [wt loss (uninh.) – wt loss (inh.)] / wt loss (uninh.)] *x* **100……..3**

Where,
wt loss (uninh) and wt loss (inh.) are the values of weight loss without and with inhibitor, respectively.
Also percentage protection efficiency (P %) can be calculated from the corrosion rate data of the tested carbon steel without $R_{corr.}$(uninh.)or with inhibitor presence $R_{corr.}$(inh.) at a specific concentration and temperature by applying the followed equation:

P% = [R_{corr} (uninh) - R_{corr} (inh) / R_{corr} (uninh)] *x* **100 …4**

The obtained results from the weight loss tests for carbon steel specimens in sulfuric acid solution at lab temperatures were done in summer 2011 (Table -1-).

In general, the corrosion rate with (2) addition at a specific concentration and time was less that the corrosion rate without (2) addition and this conclusion can be observed is the same manner with their resulted coverage area (θ) or protection efficiencies (P%) data. The highest protection efficiencies were after 24 hrs immersion that went to less data after 120hrs immersion and then more less after 168 hrs immersion. This changing in corrosion rate (θ or P %) with time immersion is reasonable with using a diluted sulfuric acid solution (0.02N).

The reason behind these differences can be attribute to ferrous sulfate solubility, the corrosion rate [29], the differences in temperature range in lab, exposure duration, and the chemical composition of the inhibition compound that had been applied.
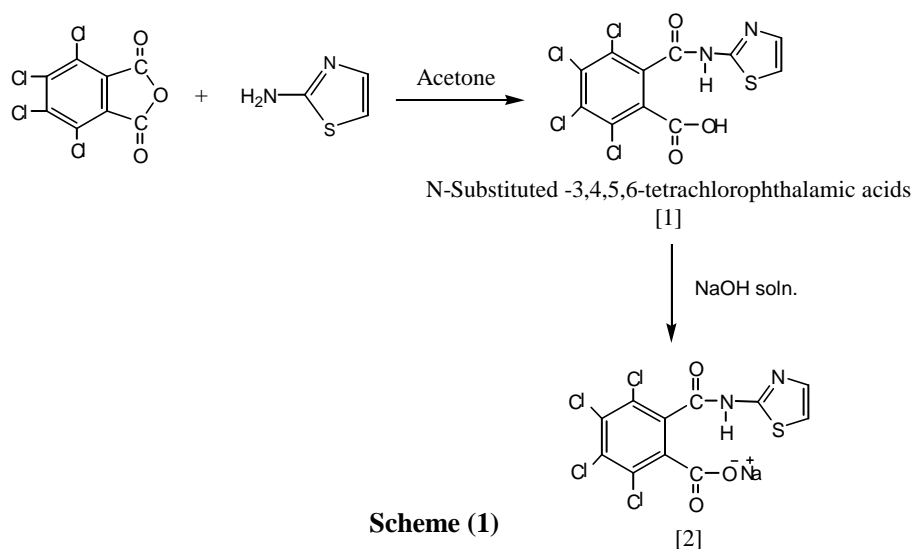
N-Substituted -3,4,5,6-tetrachlorophthalamic acids
[1]

Scheme (1)
[2]

Table 1
Gravimetric (weight loss) data for carbon steel sheets immersed in 0.02 N H_2SO_4 at lab temperature [40 ($\pm$10)] ^{o}C with different immersion times.

Comp. No.	Inhibitor Conc., ppm	Degree of surface coverage, (Percentage Protection efficiency, P%)			corrosion rate (mg.cm^{-2}.min.$^{-1}$) (x10^{-3})		
		24hrs.	120hrs.	168hrs.	24hrs.	120hrs.	168hrs.
Acid	-	-	-	-	18.1559	4.9123	3.7558
(2)	50	0.3939 (39.39)	0.1152 (11.52)	0.1106 (11.06)	11.0035	4.3464	3.3403
	100	0.6406 (64.06)	0.3008 (30.08)	0.1524 (15.24)	6.5235	3.4346	3.1831
	200	0,6493 (64.93)	0.2784 (27.84)	0.2212 (22.12)	6.3663	3.5447	2.9249

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