

A Review On Thiazole Derivatives As Corrosion Inhibitors For Metals And Their Alloys

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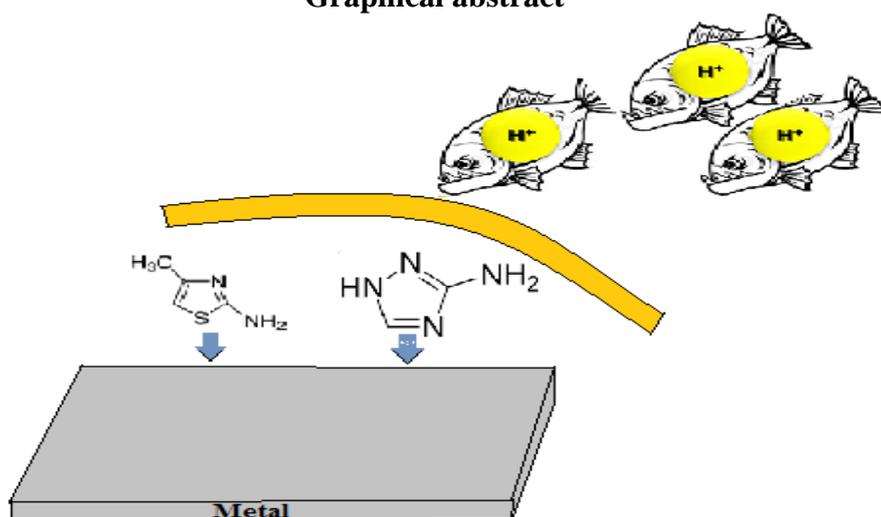
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Abstract : Innumerable organic corrosion inhibitors for various metals and their alloys have been persistently reported. The synthetic heterocyclic compounds composed of strong electronegative atoms/ hetero atoms such as oxygen, nitrogen, sulphur, phosphorus was observed to be very effective at preventing metal corrosion. A concept of studying Thiazole derivatives compounds for corrosion inhibition of metals has been formed in recent years as they contains hetero atoms, aromatic ring structure and pi bond in the structural geometry. Throughout this article, the goal is to examine the potential of thiazole derivatives as corrosion inhibitor for various metals and alloys through acidic or basic environment.

Keywords: Thiazoles; Corrosion inhibition; Metals; Alloys; Acid

Graphical abstract



1. Introduction

Thiazole is a five-member, planar, π -excessive aromatic hetero possessing a sulfur atom along a pyridine sort of nitrogen atom in 3rd place of cyclic ring system, serving as a core component for different molecules with variety of applications, especially in medicine. Several natural products which have a thiazole ring with significant therapeutic properties have been persistently reported. Thiamine, commonly recognized as B1 vitamin, has a

thiazole ring associated to 2-methylpyrimidine-4-amine as hydrochloride salt as well as shows various agricultural, industrial and biomedical activities such as , anticonvulsant, anti-microbial anticancer, anti-inflammatory, diuretic, antitubercular, antibacterial and antifungal characteristics. Some medications like ketoconazole and fluconazole reported as potential anticadio vascular agents. In addition, one of the recently processed 5-(2,4-dichlorobenzylidene)-2-(naphthalen-1-ylamino)thiazol-4(5H)-one a thiazolin-4-one derivative was reported to be extremely effective towards a series of pathogenic fungi (MIC = 0.015 $\mu\text{g} / \text{mL}$). Due to their strong chemical behavior and less toxicity, such compounds can deemed as environment friendly corrosion inhibitors for metals such as copper, iron, aluminum, zinc etc. [1]. Such compounds are mostly amphoteric, form salts of acids/bases[2]. Also, they have pi electrons which can interact with any metal or alloy's d-orbitals and thus build a protective layer or film [3]. Thus in recent years work on thiazole derivative inhibitors has been a popular trend.

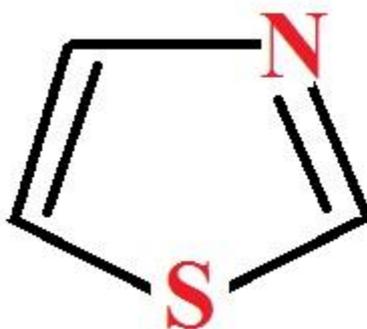


Fig.1. Basic structure of Thiazole

2.Thiazole Derivatives as Corrosion Inhibitors

2.1. Iron and Its Alloys

Iron is relatively inexpensive, high tensile metal. Thus widely used in the manufacture of machine tools, vehicles, medical instruments, large ship hulls, machine parts, as well as building pieces[4]. A mixture of iron with other elements offers advanced mechanical characteristics which are desirable for several use and applications. Major issue though is that it is poor resistant to corrosion, notably in aggressive environments. Industrial operations like de-scaling, acid cleaning, braising and excavation in oil and gas production utilize acidic solution widely so these iron, steel vessels or structures becomes more vulnerable to corrosion in these conditions[5]. Within the literature on organic corrosion inhibitors, the adsorption mechanism and the correlation between the inhibitor structures and their adsorption are listed [6]–[11]. Adsorption has been reported to rely primarily on electronic and structural characteristics of inhibitor molecule i.e. aromaticity, steric factors, functional groups, density of electrons and p orbital behavior [12]. Acid solutions are used widely in manufacturing processes. Within these conditions the corrosion of iron and its prevention is a dynamic phase issue. This is usually highly cost-effective to use organic inhibitors for mitigating mild steel corrosion in acidic environment. Over the past few years, steel inhibition in acidic solutions has also been studied extensively by various kinds of organic inhibitors.

Some thiazoles derivatives, namely 4,4'-(4(ethane-1,2-diylbis(oxy))bis(4-phenylene)dithiazol-2-amine [13], 2-(acetyl-ethoxy carbonyl-methylene)-3-phenyl-4-(phenylhydrazono)-1,3-thiazolidin-5-one [14], 2-amino-4-(4-chlorophenyl)-thiazole[15], 2-Methoxy-1,3-thiazole (MTT), 4-(4-Methylphenyl)-2-thiazolamine and Thiazole-4-carboxaldehyde (TCA)[16], 2-amino-4-methyl-thiazole[17], 2-salicylidene amino-4-phenylthiazole [18], 4-[1-aza-2-(phenyl)vinyl]-3-phenyl-2- thioxo(1,3-thiazoline-5-yl)[19]

revealed as mixed type inhibitor in H₂SO₄ and HCl media. An increase in I.E. was noted with increasing concentration of thiazole derivatives. Analyzed results from gravimetric technique and electrochemical analysis were appropriately acknowledged. Adsorption of the most of thiazole derivatives on metal surface follows Langmuir isotherm model.

Thermodynamic functions were obtained to gather valuable details about inhibition behaviour of thiazole derivatives. For greater perspective on electronic and molecular effects with inhibition efficiencies, molecular modeling has been used. Quantum chemical equations have supported the empirical findings in such investigations[20].

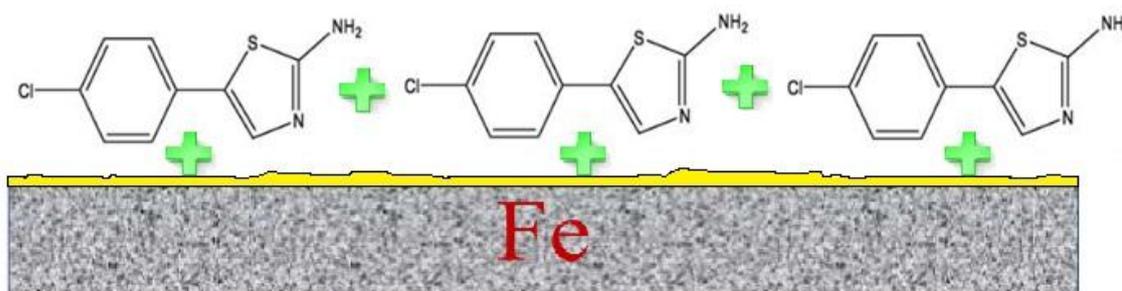


Fig.2. Adsorption of thiazole derivative 2-amino-4-(4-chlorophenyl)-thiazole on the iron surface

2.2. Copper and Its Alloys

Copper and its alloys are seeking out new application area in traditional industries. Copper is an extremely virtuous metal; although, vulnerable to acid corrosion and strong alkaline solution, notably when oxygen or oxidants are present. The deterioration of Cu is incredibly fast in the pH region around 2.5 and 5, and it is impossible to form stable surface oxide layers that can passive metal surfaces. For low acid or alkaline solutions, copper corrosion can be suppress by generating an protective layer on its surface[21]. Some derivatives of thiazole were effectively used to inhibit copper corrosion.

The analysis of thiazole derivatives for copper corrosion inhibition was conducted primarily in H₂SO₄ and HCl solutions with respect to industrial sector uses, where copper subjected to these chemicals is being used. 5-benzylidene-thiazolidine-2,4-dione [22], 2-amino-thiazole (ATZ) and 2-amino- 4,6-dimethyl-pyrimidine (ADMP)[23], 4-(2-aminothiazole-4-yl) phenol (ATP), 4,4'-(thiobis(2-aminothiazole-5,4-diyl)) diphenol (TATD) and 4-phenylthiazole-2-amine (PTA) [24], 5-(5'-methylfurfurylidene-2')-2,4-dioxotetrahydro-1,3-thiazole [25], 2-aminobenzothiazole and 2-amino-6-bromobenzothiazole[26], 5-benzylidene-2,4-thiazolidinedione[27], 5-(4'-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole[28] have been examined by several techniques such as spectroscopic, gravimetric and electrochemical techniques to investigate their inhibition efficiency against copper corrosion. Results demonstrated that with increasing the inhibitor concentration the inhibition efficiency increases and attains a maximum peak point[29]. For several experiments, activation energies are calculated by measuring temperature independence of corrosion current in inhibitor's presence/absence. Alterations in impedance parameters confirmed the inhibitor adsorption on the surface of copper, resulting in a protective layer forming[30]. In these experiments, copper surface adsorption of inhibitor observed to obeyed Langmuir adsorption isotherm[31].

Polarization curves from potentiodynamic polarization analysis reveal most of the derivatives as mixed type inhibitors. Adsorption of derivatives obeyed Langmuir's adsorption isotherm. Analysis indicates that copper corrosion inhibition was caused by thiazole derivative adsorption on the copper surface where adsorbed thiazole derivative formed Cu-complex that

suppress the chloride complex formation in copper. The experimental findings from electrochemical polarization showed the high inhibitive performance of the thiazole derivatives being studied.



Fig.3. Adsorption of thiazole derivative 5-(5'-methylfurfurylidene-2')-2,4-dioxotetrahydro-1,3-thiazole on Cu surface

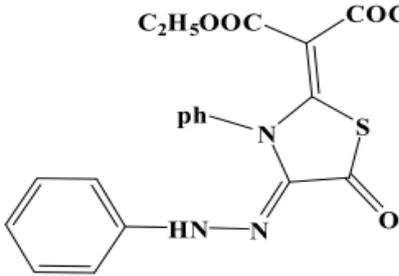
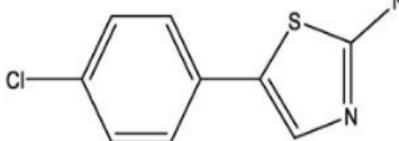
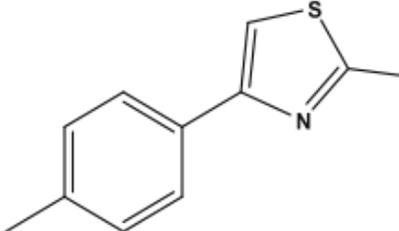
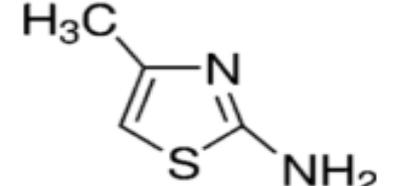
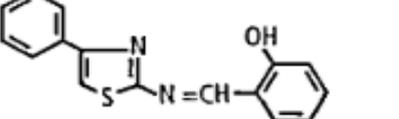
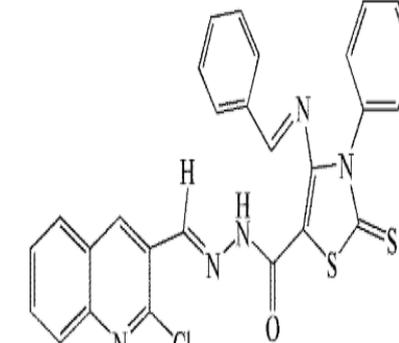
2.3. Aluminium and its Alloys

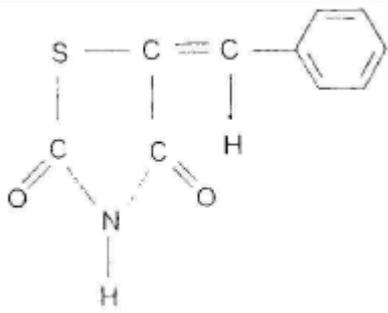
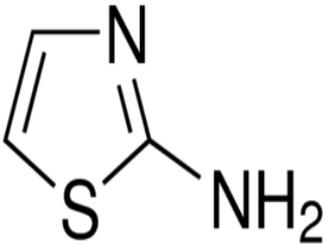
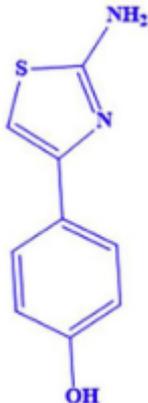
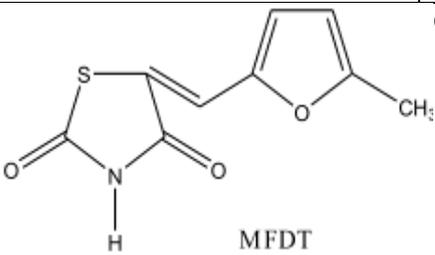
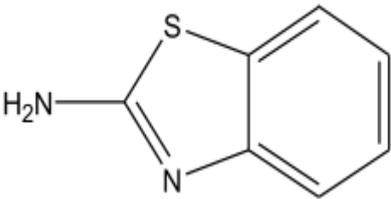
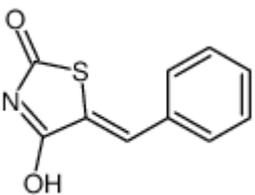
Aluminum as well as its alloys has indeed been extensively used in shipping, construction, electrical engineering, home appliances, packaging, aircraft and aircraft sectors as products. One explanation is that aluminum provides good thermal and electrical conductivity, light mass (density of 2,6 g / cm³) also it have comparatively low price and is roughly twice as efficient as iron. Furthermore, due to emergence of resistive oxide layer, aluminum displays high resistance to corrosion as it is exposed to atmosphere and other unfavorable conditions which give rise to corrosion[32]. A literature survey shows that specific organic inhibitors of corrosion are commonly seemed to avoid aluminum dissolution in basic and acidic media. The corrosion mitigation activity of thiazole derivatives was calculated by thermodynamic parameters e.g. enthalpy/ entropy of adsorption etc.

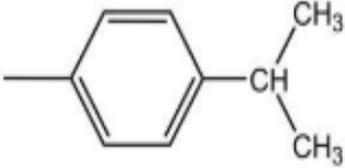
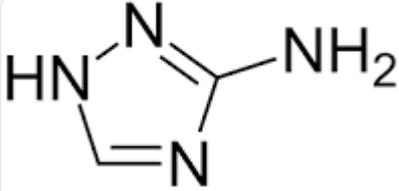
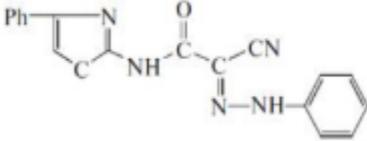
Present potential curves and gravimetric measurements revealed as 1,2,4-triazole, 3-amino-1,2,4-triazole, benzotriazole and 2-mercaptobenzothiazole[33], N-thiazolyl-2-cyanoacetamide[34], 2-amino[4-p-Hydroxyphenyl]Thiazole and 2-amino[4-p-Bromophenyl]Thiazole [35] gives the best inhibition efficiency. The adsorbability and hydrophobicity of the thiazole complexes and the stabilization of the Al-thiazole complex are the significant measures affecting the inhibition performance of thiazole derivatives within various treatments [36].

Table 1. Several derivatives of thiazole as corrosion inhibitors for many metals and alloys in acidic / basic solution

S.No	Inhibitor name	Structure	Metal	Medium	Ref(s)
1.	4,4'-(4(ethane-1,2-diylbis(oxy))bis(4-phenylene)dithiazol-2-amine		Mild steel	0.5M H ₂ SO ₄	[13]

2.	2-(acetyl-ethoxy carbonyl-methylene)-3-phenyl-4-(phenylhydrazono)-1,3-thiazolidin-5-one		Carbon steel	2M HCl	[14]
3.	2-amino-4-(4-chlorophenyl)-thiazole		Mild steel	0.5 M HCl	[15]
4.	4-(4-Methylphenyl)-2-thiazolamine		Carbon steel	0.5M H ₂ SO ₄	[16]
5.	2-amino-4-methyl-thiazole		Carbon steel	0.5M HCl	[17]
6.	2-salicylidene amino-4-phenylthiazole		Mild steel	1M HCl	[18]
7.	4-[1-aza-2-(phenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)		Carbon steel	15% HCl solution	[19]

8.	5-benzylidene-thiazolidine-2,4-dione		Copper	0.1 M Na ₂ SO ₄	[22]
9.	2-amino-thiazole		Copper	Tap water	[23]
10.	4-(2-aminothiazole-4-yl) phenol		Copper	1M HCl	[24]
11.	MFDT	 MFDT	Copper	0.1 M dm ⁻³ Na ₂ SO ₄	[25]
12.	2-aminobenzothiazole		Copper	3% NaCl solution	[26]
13.	5-benzylidene-2,4-thiazolidinedione		Copper	0.1 M Na ₂ SO ₄	[27]

14.	(5-(4'-isopropylbenzylidene-2,4)-dioxotetrahydro-1,3-thiazole)		Cu	0.1 M Na ₂ SO ₄	[28]-[34]
15.	3-amino-1,2,4-triazole		AA2024 aluminium alloy	0.005 M NaCl	[35]-[42]
16.	N-thiazolyl-2-cyanoacetamide		Aluminium	0.01M NaOH	[43]-[50]
17.	2-amino[4-p-Hydroxyphenyl]Thiazole		Aluminium	0.02 M NaOH	[51]-[58]

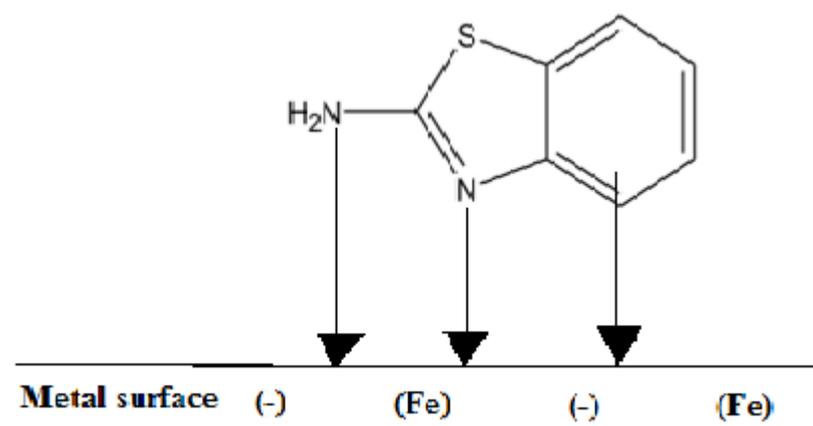


Fig.4. Adsorption of inhibitor molecule on metallic surface

3. Conclusion

Thiazole derivatives as corrosion inhibitors for various metals have been examined in various media. Thiazole derivatives are proven to be efficient inhibitors of corrosion due to the special structural properties of thiazole derivatives such as hetero atoms, aromatic ring structure and pi bond in the structural geometry. Assay from the corrosion analysis using various techniques revealed that these derivatives are strong inhibitors of corrosion (Table 1). The analyses have found that most of thiazole derivatives act as a mixed form inhibitor. It

was also noted that the inhibition of corrosion usually rises with increasing inhibitor concentration and follows Langmuir adsorption isotherm.

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