

Thiosemicarbazone Derivatives as Corrosion Inhibitor: A Review



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Abstract

The inhibiting effect of thiosemicarbazone derivatives towards the corrosion of different metals and alloys in different medium has been reviewed in this paper. The presence of hetero- atoms like S, N etc and π -electrons in form of conjugation in their structure improve corrosion inhibition efficiency of thiosemicarbazone derivatives. Their inhibition capability was studied using weight loss method and electrochemical measurements (potentiodynamic polarization, SEM and EIS). The inhibition efficiencies obtained from all methods employed are in good agreement and inhibition efficiencies increased with the concentration of inhibitors. Kinetic and thermodynamic parameters provide valuable information about the mechanism of corrosion inhibition.

Keywords: Corrosion, thiosemicarbazone(TSC), Inhibitor, Potentiodynamic polarisation, SEM and EIS.

Introduction

Corrosion is the deterioration or destruction of metals and alloys by the reaction with its environment. The environment could be of any type such as atmosphere, water, seawater, acid alkaline, steam, gases, soil and liquid metals etc. Corrosion is an electrochemical process in which pure metal surface act as anode and impurities act as cathode and a mini electrochemical cell develop on the surface of metal [1]. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Mostly metals like Fe, Cu and Al are major part of infrastructure. Corrosion is one of the major causes of material failure and hence leads to a huge coast to our society. Corrosion has a huge economic and environmental impact on all facets of national infrastructure [2]. Prevention would be more practical and achievable than complete elimination. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. The corrosion inhibitors protect the metal surface from its environment. Actually corrosion inhibitors adsorbed at the metal surface and form a stable metal complex protecting layer or barrier which protect metal surface from its environment. Organic compounds containing a heteroatom (N, O and S) in their structure act as good corrosion inhibitors. The corrosion inhibitor efficiency of organic inhibitor are depends on the chemical structure and physiochemical properties of the compound like functional groups, electron density at the donor atom, p -orbital character, and the electronic structure of the molecule [3]. Most of organic inhibitors are expensive, toxic and have negative effect on the environment this properties restrict its use to inhibit the metal corrosion. Thus it is important and necessary to develop low cost and environmentally safe corrosion inhibitors [4-5]. For the past several decades, thiosemicarbazone and their derivatives have been investigated for biological importance and hundreds of transition-metal complexes have been prepared and structurally characterized[6]. In recent years, the efficiency of thiosemicarbazone compounds as organic corrosion inhibitors has been studied in a wide range[7-15]. The high activity and efficiency of these compounds against corrosion was due to the presence of both nitrogen and sulfur in their structures.

Review of Literature

A large number of thiosemicarbazone derivatives have been synthesized during the last decades and they are found to be effective corrosion inhibitors for different metals and alloys.

Two N(4)-substituted thiosemicarbazones, anisoin and furoin N(4)-methyl(phenyl)thiosemicarbazone have been tested by John et al. as corrosion inhibitors on mild steel in 1M HCl solution using electrochemical impedance spectroscopy, potentiodynamic polarization methods and

adsorption studies [16]. Laxmi et al. have synthesized 4-ethylcyclohexanethiosemicarbazone (ECHTSC) and investigated the corrosion inhibition efficiency towards Fe in (0.5N HCl) by the weight loss method. The protective layer of thiosemicarbazone on Fe surface was confirmed by scanning electron microscopy (SEM) [17]. Khaled et al. have investigated the Inhibition effect of 3-pyridinecarboxaldehyde thiosemicarbazone (META) on the mild steel corrosion in one molar hydrochloric acid using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) [18]. Priya et al. have studied the inhibitory effect of alkyl substituted 2,6-diphenyl piperidin-4-one with thiosemicarbazone on mild steel in 1 N sulphuric acid by using Quantum chemical calculations, electrochemical AC impedance measurements, weight loss process and potentiodynamic polarization studies[19].The inhibition effect of a new synthesized organic inhibitor , namely 1-(3-Nitrobenzylidene) Thiosemicarbazide (A) on the corrosion of mild steel in 0.5 M sulphuric acid have been investigated at room temperature using weight loss, electrochemical impedance spectroscopy(EIS) and Tafel polarization measurements[20]. The p-methoxyacetophenone thiosemicarbazone, p-methylacetophenone thiosemicarbazone and p-aminoacetophenone thiosemicarbazone tested towards nickel corrosion in 1.0 M HNO₃ solutions using electrochemical techniques (polarization and impedance) [21].

Okafor et al. have investigated the inhibition effect of 2-acetylpyridine-(4-phenyl) thiosemicarbazone (2AP4PTSC), 2-acetylpyridine (4methyl) thiosemicarbazone (2AP4MTSC), 2-acetylpyridinethiosemicarbazone (2APTSC) on the mild steel in 5M H₂SO₄ [22] .The corrosion inhibition of Fe78B13Si9 glassy alloy by some thiosemicarbazone derivatives in 0.2 M Na₂SO₄ solution containing 10% MeOH has been studied by using electrochemical (polarization and impedance) measurements [10]. Albuquerque et al. synthesised 2-hydroxybenzaldehyde-thiosemicarbazone (THIO-6)

and investigated anticorrosive activity against AISI 1020 carbon steel in acid medium by using the electrochemical methods Potentiodynamic Polarization and Impedance Electrochemical Spectroscopy [23]. Corrosion inhibition of mild steel in HCL by pyridoxalthiosemicarbazone (PHTSC) and anisaldehyde thiosemicarbazone (ATSC) at 303-333K and concentration of .0001-0.0005 has been studied using weight loss technique [24]. Khaled have investigated the inhibition effect of some thiosemicarbazones on aluminium corrosion in 1.0HNO₃ [25]. Three thiosemicarbazone derivatives, namely (E)-2-(2-hydroxybenzylidene) hydrazinecarbothioamide (MHC), (E)-2-(2,4-dihydroxybenzylidene) hydrazinecarbothioamide (DHC) and (E)-2-(2,3,4 trihydroxybenzylidene) hydrazinecarbothioamide(THC) were synthesized and their corrosion inhibition action on 2024-T3 aluminum alloy were studied in 3.5% NaCl solution[26]. Three organic inhibitors namely, 1-vanilinthiosemicarbazone (VTS),1-Salicylaldehydethiosemicarbazone(STS) and 1-Dimethylaminobenzaldehydethiosemicarbazone have been synthesized by Quraishi et al. and their inhibiting ability studied towards mild steel in acidic medium (20% formic acid and 20% acetic acid) by using weight loss and potentiodynamic polarization method[27]. The acid corrosion inhibition technique of mild-steel in 1N sulphuric acid by a part of alkyl substituted 2, 6-diphenyl piperidin-4-one with thiosemicarbazone has been observed by quantum chemical calculations, electrochemical AC impedance measurements, weight loss process and potentiodynamic polarization studies. Results show that substituted γ -2, c-6-diphenyl piperidin-4-ones with thiosemicarbazone act as perfect corrosion inhibitors and their inhibition efficiency increase with the addition of inhibitors [28]. Kashar et al. have synthesized two furan and naphthalene based thiosemicarbazone derivatives and studied the inhibition efficiency towards cast iron in1.0M H₂SO₄ by using electrochemical methods [29].

Table 1: List of Thiosemicarbazone Derivatives Used As Corrosion Inhibitors in Different Media

S.No.	Metal/Alloy	Medium	Name of Inhibitor	Author/Year
1	Fe	0.5M HCL	4-ethoxycyclohexano thiosemicarbazone(4ETCHTSC)	Meena et al./2018
2	Mild Steel	1M HCl	3-pyridinecarboxyaldehydeTSC(3PDCTSC)	Khaled et al./2010
3	Ni	1M HNO ₃	p-aminoacetophenone thiosemicarbazone(PAACPTSC) p-methylacetophenone thiosemicarbazone(PMACTSC) p-methoxyacetophenonethiosemicarbazone(PMTACPTSC)	Khaled et al./2011
4	Mild steel	5M H ₂ SO ₄	2-acetylpyridine-(4-phenyl)TSC(2AP4PTSC) 2-acetylpyridine-(4-methyl)TSC(2AP4MTSC) 2-acetylpyridinethiosemicarbazone(2APTSC)	Okafor et al./2008
5	Fe2B13Si9 Glassy alloy	0.2M Na ₂ SO ₄	4-methylacetophenonethiosemicarbazone(4MACPTSC) 4-methoxyacetophenonethiosemicarbazone(4MTACPTSC) Benzaldehydethiosemicarbazone(BZTSC) 4-methoxybenzaldehydethiosemicarbazone(4MTBZTSC) 4-ethylbenzaldehydethiosemicarbazone(4ETBZTSC) 4-bromobezaldehydethiosemicarbazone(4BRBZTSC)	Arab et al./2008
6	Mild Steel	HCL	Anisoin N(4)-methyl(phenyl)TSC(AMPTSC) Furoin N(4)-methyl(phenyl)TSC(FMPTSC)	John et al./2016
7	Steel	1M HCL	2-hydroxy benzaldehydeTSC(2-HBTSC)	Albuquerque et

				al./2016
8	Mild Steel	HCL	AnisaldehydeTSC	Ita et al./2007
9	Aluminium	1M HNO ₃	3-pyridinecarboxyaldehydeTSC(META) IsonicotinaldehydeTSC(PARA) 2-pyridinecarboxyaldehydeTSC(ORTHO)	Khaled/2010
10	Mild Steel	20% Formic acid	1-VanilinTSC(VTS) 1-SalicylaldehydeTSC(STS) 1-DimethylaminobenzaldehydeTSC(DTS)	Quraishi et al./2002
11	Mild Steel	20% Acetic acid	1-VanilinTSC(VTS) 1-SalicylaldehydeTSC(STS) 1-DimethylaminobenzaldehydeTSC(DTS)	Quraishi et al./2002
12	2024-T3 Aluminium	3.5% NaCl	(E)-2-(2-hydroxybenzylidene)TSC (E)-2-(2,4-dihydroxybenzylidene)TSC (E)-2-(2,3,4-trihydroxybenzylidene)TSC	Prakashaiah et al./2018
13	Steel	H ₃ PO ₄	CinnamaldehydeTSC	Khamis et al./2000
14	Mild Steel	HCL	4-FluorobenzaldehydeTSC 4-Fluorobenzaldehyde-2-methylTSC	Tarasconi et al./2015
15	18Ni 250 Steel	0.5H ₂ SO ₄	3,4-dimethoxybenzadehydeTSC	Poornima et al./2011
16	Mild Steel	1N H ₂ SO ₄	3-methyl-2,6-diphenylpiperidine-4-oneTSC 3-ethyl-1-methyl-2,6-diphenylpiperidine-4-oneTSC 3-ethyl -2,6-diphenylpiperidine-4-oneTSC	Priya et al./2018
17	Mild steel	0.5M H ₂ SO ₄	1-(3-nitrobenzylidene)TSC(1-3NBTSC)	Dadgarinezhed et al./2011
18	Cast iron	1.0M H ₂ SO ₄	1-(1-(5-hydroxy-2-methylbenzofuran-3-yl) ethylidene) thiosemicarbazone2a(L ¹) 1-(1-(5-hydroxy-2-methylnaphtho[1,2-b]furan3yl)ethylidene)thiosemicarbazone 2b(L ²)	Kashar et al./2017

Synthesis of thiosemicarbazone derivatives

The thiosemicarbazone derivatives reviewed in this review were prepared by refluxing (for some hour and min.) in ethanol an equimolar amount of carbonyl compounds and thiosemicarbazone by researcher. The structures of the derivatives were established by UV, IR, ¹H-NMR and ¹³C-NMR.

The thiosemicarbazone (4-ethylcyclohexanonethiosemicarbazone (ECHTSC)) was synthesized [30-31] by Meena et al. from 4-ethylcyclohexanone and Thiosemicarbazide in equal molar ratio in methanol. The structure of compound was characterized by IR studies. Absence of a u(C=O) band (1745 cm⁻¹) of ketone and presence of u(C=N) band occurred at 1622-1632 cm⁻¹ in the spectra of thiosemicarbazone indicating the condensation between ketonic group of 4-ethylcyclohexanone and amino group of Thiosemicarbazide.

John et al. (2016) have synthesized two thiosemicarbazone derivatives namely AMPTSC and FMTSC. Anisoin (0.01 mol, 2.7 g) (Sigma Aldrich) and MPTSC (0.01 mol, 1.8 g) in 50 cm³ ethanol were refluxed well for 2 h, in the presence of P-toluene sulfuric acid as catalyst, on a water bath. The mixture was concentrated to diminish the volume to half and kept for half an hour. The yellow precipitate formed is filtered and washed with cold ethanol. (Yield: 1.45 g (81%), mp 116 °C). MPTSC (0.005 M, 0.905 g) dissolved in hot ethanol (20 cm³) was added to a solution of furoin (0.005 M, 0.96 g) (Sigma Aldrich) in hot ethanol. Two drops of concentrated HCl was added during onset of the reaction. After refluxing for 2 h on a water bath, the mixture was cooled to room temperature. The product furoin N (4)-(methyl)

phenylthiosemicarbazone was collected by suction filtration, washed with ethanol and dried (Yield: 0.76 g (85%); m.p-165 °C).

A mixture of 1-(1-(5-hydroxy-2-methylbenzofuran-3-yl) ethylidene) (1a) or 1-(1-(5-hydroxy-2-methylnaphtho [1, 2-b] furan-3-yl) ethylidene) (1b) (0.01mol) and thiosemicarbazide (0.01mol) was added in a 20ml ethanol. The mixture was refluxed for 8h, concentrated, and cooled. The precipitate which was formed was filtered off, dried, and was

Crystallized from a given solvent to give thiosemicarbazones 2a (L¹) or 2b (L²) as white needles. 1-(1-(5-hydroxy-2-methylbenzofuran-3-yl) ethylidene) thiosemicarbazone2a (L¹) and 1-(1-(5-hydroxy-2-methylnaphtho [1, 2-b] furan3yl) ethylidene) thiosemicarbazone 2b (L²) were Recrystallize by using dilute ethanol [29].

The preparation of THIO-6 was done from equimolar quantities of 2-hydroxybenzaldehyde and thiosemicarbazide, in ethanol as solvent and catalytic quantities of concentrated sulphuric acid, at room temperature, under 6 h of magnetic agitation. Reaction was monitored by thin-layer chromatography, using ethyl: hexane acetate (7:3) as eluent. The product was recrystallized from ethanol and yielded 84%. *Characterisation*: white solid, melting point: 243-244 °C; NMR 1H (DMSO-d₆, δ): 11.31 (NH), 9.92 (OH), 8.38 (CH=N), 7.90 (H-6), 7.23 (H-4), 6.91 (H-3), 6.83 (H-5) [23].

Hot ethanolic solution (20 mL) of 3-aminoacetophenone (1.35 g, 0.01 mol) was mixed with hot ethanolic solution of thiosemicarbazide (0.91 g, 0.01 mol) in the presence of 2-3 drops of glacial acetic acid. The content was refluxed for about 2-3

hours on a water bath. On cooling the contents the brown colored compound separated out. The same was filtered, washed with 50% ethanol, recrystallised in ethanol and dried in vacuum over P₄O₁₀. Yield 85%, m.p.125 °C. Elemental analysis % found for C₉H₁₂N₄S, C, 51.90; H, 5.72; N, 26.89 and calculated %C, 51.92; H, 5.76; N, 26.92. Mass (m/z): 208 (M+) amu, FT-IR (KBr) (vmax, cm-1) Fig. 1: 1618 and 1506 for azomethine group may be assigned to symmetric or asymmetric -C=N- vibrations [26], 830(s) due to -C=S- group, 3305, 3229, 1447 and 1323 appears due to -NH₂, -NH and -C=N, NH₂ groups. 1H-NMR (DMSO, 300 MHz): δ- 2.02 ppm(t) (3H, H₃C-C-), 8.08 ppm(s) (1H, HN-CO), 3.14(d) (2H, H₂N-CO), 7.47-6.39 ppm(m) (4H, -ph-), 4.83 ppm(d) (2H, -ph-NH₂) [35].

Proposed Methodology

Different methods have been used to determine the inhibition efficiency of different thiosemicarbazone derivatives by Weight loss technique, Potentiodynamic polarization measurements, electrochemical impedance spectroscopy (EIS) [10, 16-29] and SEM [16-18].

Weight Loss Measurements

Rectangular specimens of metals/alloy containing a small hole near the upper edge were used for the determination of corrosion rates. The solutions of acids were prepared using doubly distilled water. Each specimen was suspended by a V-shaped glass hook made by fine capillary glass tube and immersed in a glass beaker containing 50ml of test solution at room temperature. After the exposure of sufficient time the test specimen was taken out, cleaned under running water and finally dried firstly with filter paper and secondly desiccator. The percentage corrosion inhibition efficiency was calculated by equation (1).

$$IE/\% = 100 (\Delta M_U - \Delta M_i) / \Delta M_U \dots\dots\dots (1)$$

Where, ΔM_U = Mass loss of metal in uninhibited solution.

ΔM_i= Mass loss of metal in inhibited solution.

Electrochemical Studies

The electrochemical measurements were performed in a typical three-compartment glass cell

Table 2: For the various thiosemicarbazone derivatives the values of corrosion potential (E_{corr}), corrosion current densities (I_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), inhibition efficiency (IE %), double layer capacitance (C_{dl}), Rct (charge transfer), corrosion rate and inhibition efficiency were calculated

TSC derivatives	Inhibitor conc.	-E _{corr} (mV vs SCE)	I _{corr} (Acm ⁻²)	β _a [mV dec ⁻¹]	β _c [mV dec ⁻¹]	IE [%]	Corr. rate(mmpy)	R _{ct} (Ωcm ²)	C _{dl} [F cm-2]	IE [%]
01 TS	blank	524	4.57	120	-137	104.71	32.13	0.14
	1.0(ppm)	469	0.26	35	-122	94.31	5.96	541.12	0.17	94.06
02 TS	1.0(ppm)	495	0.31	32	-35	93.22	7.10	356.79	0.11	90.99
03 TS	1.0(ppm)	478	0.39	35	-116	91.47	8.94	341.22	0.71	90.58
VTS(20%FA)	Blank	416	0.350m	8.44
	500(ppm)	404	0.039	88.85	2.60
STS(20%FA)	500(ppm)	412	0.026	92.57	2.30
DTS(20%FA)	500(ppm)	396	0.021	94.00	1.45
VTS(20% AA)	Blank	404	0.240	7.00
	500(ppm)	430	0.052	78.33	2.96

consisted of the metal/alloy specimen as working electrode (WE), platinum counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode. By changing the electrode potential around the open circuit potential, potentiodynamic potential polarization curves were conducted. From tafel plot corrosion parameters such as E_{corr}, I_{corr}, β_a and β_c were recorded (table 2).

Electrochemical impedance studies

Impedance measurements were carried out in frequency range from 100 kHz to 0.1Hz with amplitude of 5 mV peak to peak using Ac signals at open circuit potential. The experimental impedance was analyzed and interpreted based on the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the charge transfer resistance R_{ct} (diameter of high-frequency loop) and the double layer capacity C_{dl}. The charge transfer resistance (R_{ct}) values were calculated (table 2) from the difference in the Nyquist plots at low and high frequencies. Therefore, the inhibition efficiency (IE %) calculated from the charge- transfer resistance according to Eq. (2) [10, 16, 18, 23, 32]

$$IE\% = [(R_{ct} - R_{ct}^0) / R_{ct}] 100 \dots\dots\dots (2)$$

Where R_{ct} and R_{ct}⁰ are charge-transfer resistances in the presence and absence of inhibitor respectively. The double layer capacitance values (C_{dl}) was calculated using equation (3) [33].

$$C_{dl} = 1/\omega R_{ct} = 1/2\pi f_{max} R_{ct} \dots\dots\dots (3)$$

Where, f_{max} = The frequency at the maximum in the Nyquist plot.

R_{ct} = the values of charge transfer resistance.

C_{dl} = double layer capacitance obtained from the Nyquist plots and the calculated inhibition efficiency values

Surface Morphological Studies

The surface morphology of the formed layers on the metal/alloy surface after its immersion in the solutions of acidic or different medium in the absence and in the presence of the thiosemicarbazone derivatives (at various concentrations) were carried out by scanning electron microscope (SEM).

VTS(20% AA)	500(ppm)	440	0.048	80.00	2.78
VTS(20% AA)	500(ppm)	422	0.031	87.08	2.51
2-HBTSC	Blank	444	1.91	102.02	96.01	96.19
	40x10 ⁻⁵	444	0.11	94.62	69.99	94	1745.20	13.8	94
META	blank	531	149μ	107	147	68.24mpy
	10 ⁻² M	534	12μ	105	149	92	5.38
PAACTSC	blank	19.8	527 μ	169.1	223.7mpy
	10 ⁻² M	118.3	115.0	179.7	78.2	48.79
PMACTSC	10 ⁻² M	22.1	54.3	166.1	89.7	23.07
PMTACPTSC	10 ⁻² M	22.3	40.1	171.4	92.4	17.1
AMPTSC	blank	500	2.4247 m	107	-172	28.102
	100 ppm	480	0.2383m	51	-74	90.17	2.7626
FMPTSC	100 ppm	551	0.0201m	32	-53	99.17	0.2332
1-3NBTSC	Blank	118	8.88
	100(ppm)	513	22.80	98.07	431.7	75.66	97.94
2a(L ¹)	blank	455	310.5 μ	32	34	146.9	6.576
	.005M	468	56.5	45	39	81.81	28.0	62.9	84.81
2b(L ²)	.005M	459	122.5 μ	37	42	60.54	58.7	17.44	79.96

Results and Discussion

Weight Loss Measurements

Corrosion rate and inhibition efficiency of reported thiosemicarbazone derivatives (table1) in different concentration and in different media were studied. Result obtained through weight loss technique reveals that that corrosion rate values decrease as the concentration of inhibitor increases. Consequently, inhibition efficiency values increase with the increase the concentration of inhibitor. This is due to the adsorption of inhibitor on the metal/alloy surface) [10, 16-29].

Electrochemical Studies

It is clear from the potentiodynamic results reported in (table2) that the presence of thiosemicarbazone derivatives in different media decreases the corrosion rate. The cathodic as well as the anodic reactions are markedly affected by the inhibitor toward lower current densities. The decrease in I_{corr} value is due to the adsorption of the inhibitor molecules. The values of β_a and β_c changed slightly with increasing inhibitor concentration indicated the influence of these compounds on the kinetics of metal dissolution. Due to the presence of hetero-atoms (N, S etc.) in the studied compound for making adsorption, they may act as potential inhibitors. According to Ferreira et al.[34], if the displacement in corrosion potential is more than 85mV with respect to corrosion potential of the blank solution, the inhibitor are considered as mixed inhibitor.

Electrochemical Impedance Studies

It is apparent from (table 2) that the value of R_{ct} increased with increasing concentration of inhibitors. The increase in R_{ct} values is due to the formation of an insulating protective film at the metal or solution interface so that the (IE_{EIS} %) inhibition efficiency increased. On the contrary, the value of C_{dl} decreased upon the addition of the inhibitor, suggesting, a decrease in the local dielectric constant and/or an increase in the thickness of the electrical

double layer, indicating the formation of a protective layer on the metal/alloy [10, 16, 18, 23, and 32].

Thermodynamic Parameters

The values of thermodynamic parameters can provide valuable information about the mechanism of corrosion inhibition. Some thermodynamic adsorption parameters were (ΔG_{ads}, ΔH_{ads}, and ΔS_{ads}) calculated in this review from the estimated value of K_{ads} using adsorption isotherms at different temperatures. The Langmuir's isotherm for the adsorbed layers is given by the equation.

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \dots \dots \dots (4)$$

Where K_{ads} is the equilibrium constant of the adsorption/desorption process, C_{inh} is the concentration of inhibitor and θ surface coverage area.

Adsorption equilibrium constant [K_{ads}] and free energy of adsorption [ΔG_{ads}] were calculated using the equation

$$K_{ads} = 1/C_{inh} \times \theta/1-\theta \dots \dots \dots (5)$$

$$\Delta G^{\circ}_{ads} = -2.303RT \log [55.5K_{ads}] \dots \dots \dots (6)$$

It is well known that K_{ads} represents the strength between adsorbate and adsorbent. Large values of K_{ads} mean better inhibition efficiency of the inhibitors, i.e. strong electrical interaction between the double-layer existing at the phase boundary and the adsorbing inhibitor molecules. Small values of K_{ads}, however, reveal that such interactions between adsorbing inhibitor molecules and the metal surface are weaker, indicating that the inhibitor molecules are easily removable by the solvent molecules from the metal surface. The negative values of ΔG^o_{ads} indicate that the adsorption of compound on metal/alloy is proceeding spontaneously and is accompanied by a highly efficient (10, 13, 17-18, 22-23, 27). Higher values of E_a and ΔH in the presence of inhibitor indicate more energy is required for dissolution of the mild steel in 1.0 M HCl in presence of (META).

Kinetic Parameters

The kinetic parameter (table 3) provides information about rate of corrosion reaction in presence of inhibitors. The corrosion reaction affected by Temperature also, it increases the energy of the reacted species, as a result, chemical reaction get much faster. The dependence of corrosion rate (k) on the temperature can be expressed by Arrhenius equation 7

$$K = A \exp(-E_a/RT) \dots\dots\dots (7)$$

Where, E_a is the apparent activation energy, A is the pre- exponential factor and k is the corrosion rate. Enthalpy and entropy of activation (ΔH^* , ΔS^*) of the corrosion process were calculated from the transition state theory as given from eq. 8

$$K = (RT/h) \exp(\Delta S^*/R) \exp(\Delta H^*/RT) \dots\dots\dots (8)$$

Where, h is Plank's constant, N is Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. The entropy of activation (ΔS^*) in the absence and presence of inhibitor has large and negative values, this indicates that the activated complex in the rate determining step represents an association rather than dissociation, meaning that, a decrease in disordering takes place on going from reactants to the activated complex. Higher values of E_a and ΔH^* in the presence of inhibitor indicate more energy is required for dissolution of the metal/alloy in presence of thiosemicarbazone derivatives [18].

Surface morphological studies

Table 3: for the Various Thiosemicarbazoe Derivatives Thermodynamic and Kinetic Parameters Were Calculated

TSC	Inhib _{conc}	K_{ads}	ΔG_{ads} (KJmol ⁻¹)	E_a (kJmol ⁻¹)	ΔS^* (J K ⁻¹ mol ⁻¹)	ΔH^* (kJmol ⁻¹)	Corrosion rate(mmpy)	IE [%]
3PDCTSC	blank	-65.617	-196.3	18.9	105
	0.2M	-106.25	-182.2	42.3	0.05	95
DTS(20%FA)	Blank	22.09	8.44
	500(ppm)	-4.76	17.22	1.45	94.0
DTS(20% AA)	Blank	18.96	7.00
	500(ppm)	-5.04	8.11	2.51	87.08
2-HBTSC	40(ppm)	38.98X10 ³	-36.00	94
4ETCHTSC (16hr immersion time)	blank	3.395
	.04M	238.095	-24.227	0.578	82.96
PAACTSC	blank	223.7mmpy
	10 ⁻² M	-84.4	48.79	78.2
PMACTSC	10 ⁻² M	-78.25	23.07	89.7
PMTACPTSC	10 ⁻² M	22.3	-76.5	17.1	92.4
4MACPTSC	1.50X10 ⁻⁴ M	4606.11	-37.16	88.76
4MTACPTSC	1.00*10 ⁻⁴ M	96284.24	-39.01	89.29
BZTSC	2.0*10 ⁻⁴ M	53999.21	-37.55	86.29
4MTBZTSC	1.50*10 ⁻⁴ M	66546.72	-38.08	90.44
4ETBZTSC	3*10 ⁻⁴ M	55346.55	-37.61	94.01
4BRBZTSC	2.0*10 ⁻⁴ M	30705.56	-36.130	87.50
2AP4PTSC	1*10 ⁻⁵ M	110.3	0.074	95.2
2AP4MTSC	.1*10 ⁻⁵ M	114.2	0.080	94.7
2APTSC	1*10 ⁻⁵ M	66.5	0.067	94.5

The result obtained from SEM supported the parameters of weight loss measurement that there was a decrease in contact between the metal/alloy and the aggressive medium. Thus, a good absorptive protection layer formed by thiosemicarbazone derivatives efficiently inhibits the corrosion of metal/alloy [16-18].

Conclusion

It is clear that from above study the thiosemicarbazones play an important role in corrosion inhibition of metals/alloys in different media. The most effective corrosion inhibitors are those compounds which containing hetero atoms like nitrogen, sulphur as well as aromatic rings. Result obtained from the electrochemical techniques show that all the reported thiosemicarbazone derivatives acting as good corrosion inhibitors and behaves as mixed type legend. Impedance result support the formation of an insulating protective film at the metal/alloy surface. The adsorption of thiosemicarbazone derivatives on different metals/alloy obey Langmuir's adsorption isotherm. From the weight loss technique it is evident that with the increase in the concentration of inhibitor, value of corrosion rate decreases and inhibiting efficiency increases. The negative values of ΔG^0_{ads} indicate that the adsorption of compound on metal/alloy is proceeding spontaneously. From review it is clear that thiosemicarbazone derivatives easily synthesized in laboratory.

Endnotes

1. Rani B E and Basu B B J, *International Journal of Corrosion*, 2012(2012) 1-15.
2. Hoar T P, Mears D C and Rothwell G P, *Corrosion Science*, 5(1965) 279-289.
3. Negam N A, Yousef M A and Tawfik, *Recent Patents on Corrosion Science*, 3(2013) 1
4. Lotto R T, Lotto C A and Popoola A P I, *Journal of Materials and Environmental Science*, 3(2012) 885-894.
5. Ladha D G, Naik U J and Shah N K, *Journal of Materials and Environmental Science*, 4(2013) 701-708.
6. Lobana D G, Sharma R, Bawa G and Khanna S, *Coordination Chemistry Review*, (2009) 253- 977.
7. Poomima T, Nayak J and Shetty A N, *Journal of Metallurgy*, 2012(2012) 13.
8. Yurt A, Bereket G, Kivrak A, Balaban A and Erk B, *Journal of Applied Electrochemistry*, 35(2005) 1025-1032.
9. Ita B I and Offiong O E, *Material Chemistry and Physics*, 70(2001) 330-335.
10. Arab S T and Emran K M, *Materials Letters*, 62(2008) 1022-1032.
11. Kandemirli F and Sagdinc S, *Corrosion Science*, 49(2007) 2118-2130.
12. Jacob K S and Parameswaran G, *Corrosion Science*, 52(2010) 224-228.
13. Khaled K F, *Electrochimical Acta*, 55(2010) 5375-5383.
14. Mohan P and Kalaigan G P, *Journal of Material Science and Technology*, 29(2013) 1096-1100.
15. Xu B, Yang W, Liu Y, Yin X, Gong W and Chen Y, *Corrosion Science*, 78 (2014) 260-268.
16. John S, Jeevana R, Aravindashan K K and Joseph A, *Egyptian Journal of Petroleum*, 26(2) (2017) 405-412.
17. Meena L, Choudhary P, Varshney A K and varshney S, *International Journal of Chem. Tech Research*, 11(07)(2018) 337-346.
18. Khaled K F, Elhabib O A, El-Mghraby A and Ibrahim O B, *Journal of Materials and environmental Science*, 1(3) (2010) 139-150.
19. Shanmuga P V, Rani C U, Balachandran V and Velrani S, *Journal of Science and Technology*, 10(01) (2018) 44-52.
20. Dadgarinezhad A and Baghaei F, *Gazi University Journal of Science*, 24(2) (2011) 219-226.
21. Khaled K F, *Journal of Applied Electrochemistry*, 41(4) (2011) 423-433.
22. Okafor P C, Oguzie E E, Iniamage, Ikpi M E and Ekpe U J, *Global Journal of Pure and Applied Sciences*, 14(1) (2008) 89-95.
23. Albuquerque M A, De Oliveira M C C and Echevarria A, *International Journal of Electrochemical Science*, 12(2017) 852-860.
24. Ita B I, Offiang O E, Abakedi O U and Alobi N O, *Journal of Scientific & Industrial Research*, 66(2007) 919-922.
25. Khaled K F, *Corrosion Science*, 52(2010) 2905-2916.
26. Prakashaiah B G, Kumara D V, Pandith A A, Shetty A N and Rani B E A, *Corrosion Science*, (2018).
27. Quraishi M A, Jamal D and Luqman M, *Indian Journal of Chemical Technology*, 9(2002) 479-483.
28. Priya V S, Rani C V, Balachandran V and Velrani S, *Journal of Science and Technology*, 10(1) (2018) 44-52.
29. Kashar T I, Motaal M A, Emran K and Sukar N A, *European Scientific Journal*, 13(3)(2017) 249-278.
30. Sangtyani R, Rawat J, Verma P S, Varshney A K and Varshney S, *Journal of Indian Chemical Society*, 88(2011) 1553.
31. Reddy K H, Reddy P S and Babu P R, *Transition Material Chemistry*, 25(2000) 154.
32. Ahamad I, Prasad R and Quraisi M A, *Corrosion Science*, 52(2010) 1472-1481.
33. Nazeer A A, El-Abbasy H M and Fouda A S, *Research on Chemical intermediates*, 39(2013) 921-939.
34. Bentiss F, Jama C, Mernari B, Attari H E, El Kadi L, Lebrini M, Traisnel M and Lagrenee M, *Corrosion Science*, 51(2009) 1628-1635.
35. Tomar P K, Chandra S, Malik A, Kumar A and Kumar A, *Analytical & Bio analytical electrochemistry*, 3(2)(2011) 119-133.