

Synthesis and Characterization of Benzothiazol Derivative as a Corrosion Inhibitor for Carbon Steel in Seawater

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Abstract

2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile derivative was prepared and characterized using thin liquid chromatography, FTIR, ^1H NMR and ^{13}C NMR. The corrosion protectiveness, kinetics, and thermodynamics of the prepared derivative as inhibitor in artificial sea water/carbon steel (CK45) system were studied. Three concentrations of the prepared inhibitor were examined, namely, 10, 100, and 1000 ppm; protection efficiencies of 23% to 73% were recorded. It was found that the experimental data obtained from polarization reading could be fitted by Langmuir isotherm and Frumkin's isotherm; the best fit adsorption isotherm was the Frumkin adsorption isotherm. The small negative value of ΔG_{ads} indicates the spontaneity of a physical adsorption process and the stability of the adsorbed layer on the carbon steel surface. Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation in absence and in presence of the inhibitors gives some insight into the possible inhibition mechanism.

Keywords

Corrosion Inhibition, Benzothiazole Derivative, Corrosion Kinetics

1. Introduction

Seawater is one of the most corroded and most abundant naturally occurring electrolytes, covering about 70% of the earth's surface. The corrosivity of the seawater is reflected by the fact that most of the common structural metals and alloys are attacked by this liquid or its surrounding [1]. Carbon steel is the most versatile, least ex-

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pensive and widely used engineering material which has found extensive application in various industries [2]. It is used in large tonnages in marine applications, nuclear power and fossil fuel power plant, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction as well as metal processing equipment. However, the corrosion resistance of carbon steel is relatively limited. This causes many corrosion problems to be arising in the related industries [3]-[5]. Using inhibitors is an important method for protecting materials against corrosion [6]-[8]. Various types of organic inhibitors have been published [9]. The molecules most often used as corrosion inhibitors are nitrogen, sulfur, oxygen and phosphorus compound [10]-[13]. Nitrogen and sulfur as constituent atoms were studied as corrosion inhibitor in HCl medium [14] [15].

Corrosion inhibition efficiency of organic compounds is related to their adsorption properties [16]. The adsorption of these molecules depends mainly on certain physicochemical properties of the inhibitor molecule such as, functional groups, steric factor, aromaticity, electron density at the donor atoms and π orbital character of donating electrons and electronic structure of the molecules [17]-[20]. Adsorption can be described by two main types of interaction as follows [21] [22].

1) Physisorption involves electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at metal/solution interface. In this case, the heat of adsorption is low and therefore this type of adsorption is stable only at relatively low temperature.

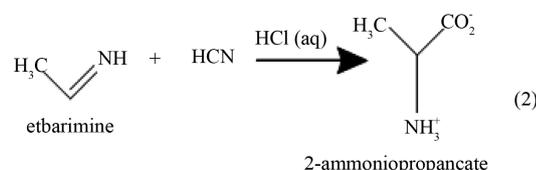
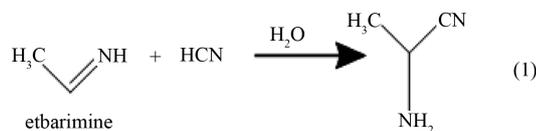
2) Chemisorption involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type bond. In fact, electron transfer is typically for transition metals having vacant low-energy electron orbital. Chemisorption is typified by much stronger adsorption energy than physical adsorption. Such a bond is therefore more stable at higher temperatures. Molecules that contain both nitrogen and sulfur in their structure are of particular importance, since these provide an excellent inhibition in comparison to that containing only sulfur or nitrogen atoms [23] [24]. Organic molecules could be adsorbed on the metal surface by one of the four following mechanisms.

1) Electrostatic interaction between charged surface of metal and the charge of the inhibitor.

2) Interaction of unshared electron pairs in the inhibitor molecule with the metal.

3) Interaction of π -electron with metal and d-A combination of the 1) - 3) types [25] [26]. The purpose of this paper is to evaluate a new synthesis of benzothiazol derivative [2-(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxyphenyl) acetonitrile] as corrosion inhibitor for carbon steel in artificial sea water (3.5% NaCl). The adsorption and inhibition efficiency of this inhibitor were investigated and thermodynamic adsorption parameters in absence and present of this inhibitor were calculated.

α -Amino nitriles have occupied an important, although often understated, position in organic chemistry ever since Strecker's original report in 1850 on the three component reaction. Now bear his name, among aldehydes, ammonia and hydrogen cyanide [27]. α -amino nitriles are useful intermediates for the synthesis of amino acids [28] [29]. These bifunctional compounds have subsequently been shown to be versatile intermediates in a number of synthetic applications. Strecker synthesis and subsequent nitrile hydrolysis are indeed a very convenient method for accessing non-proteinogenic α -amino acids [30]. The classical Strecker reaction was clarified below:



2. Experimental

2.1. Instruments and Materials

All the chemicals and solvents which are used for the synthesis were of reagent grade and obtained commer-

cially from British Drug House (BDH). Melting point was determined on a Gillenkamp melting point apparatus. The infrared spectra of the ligand and its complexes were recorded in the range (4000 - 400) cm^{-1} on a Shimadzu (8300) FTIR Spectrophotometer, using CsI pellets. Elemental analysis for carbon, hydrogen and nitrogen elements were carried out at the Euro vector-EA3000A C. H. N. Analyzer, Al al-Bayt University (Jordan). ^1H NMR and ^{13}C -NMR spectra was recorded on a make Bruker model ultrashied 300 MHz, NMR at AhlAl-Bait University (Jordan).

2.2. Preparation Method of 2-(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) Acetonitrile

A general method [31] [32] can be adopted for preparation which can be described as follows: The 2-hydroxy-benzaldehyde (1 mmol) was added to (20 ml) glacial acetic acid, p-toluene sulphonic acid was added in very small portion as catalyst, followed by addition of (1 mmol) benzothiazol-2-ylamine. The pH was adjusted to about 4 by addition of concentrated sulfuric acid drop wise to obtain Schiff base which stirred for 30 min. Potassium cyanide (2 mmol) was added to the mixture and kept under stirring for 4 days. The reaction mixture was poured into ice and then made slightly alkaline with ammonium hydroxide solution. The solid precipitate which formed was filtered, washed with water and air dried. The presence of nitrile group in the prepared α -amino nitrile was indicated by treating few amount of the sample with 10% sodium hydroxide solution, the liberation of ammonia after hydrolysis of nitrile group, which was detected by wet red litmus paper, indicating the presence of nitrile group.

2.3. Corrosion Measurement

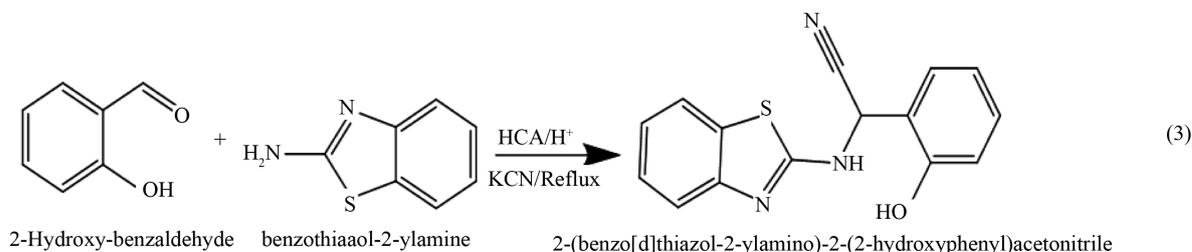
The electrolyte solution (3.5% NaCl), was prepared from reagent grade NaCl. The corrosion cell used had three electrodes, the reference electrode was a silver/silver chloride electrode., the platinum electrode was used as auxiliary electrode, and the working electrode was carbon steel specimens and the preparation procedure was as follows: thin disks with section-area of 1 cm^2 were cut from the carbon steel (CK45) sheet with chemical analysis of; C (0.45), S (<0.030), Mn (0.65), Si (0.25) (wt%) and Fe (remainder). Carbon steel disks were mechanically ground down by 1200 grit abrasive SiC papers, then washed with distilled water and methanol and dried in warm and dry air flow.

The electrochemical measurement were carried out using advanced computerized potentiostatmodel Wenking MLab-200 of Bank Elektronik-Intelligent controls GmbH (Germany) and jacketed Pyrex glass cell. Polarization curves were recorded at constant sweep rate of 2 mv/s and scanning range was from -200 to + 200 mv with respect to the open circuit potential. Before each experiment, the working electrode was immersed in the test cell for 30 min until to reach steady state condition. All tests were carried out at constant temperature (within $\pm 1^\circ\text{C}$) by controlling the cell temperature using a cooling heating circulating water bath.

3. Result and Discussion

3.1. Preparation and Identification Benzothiazol Derivative

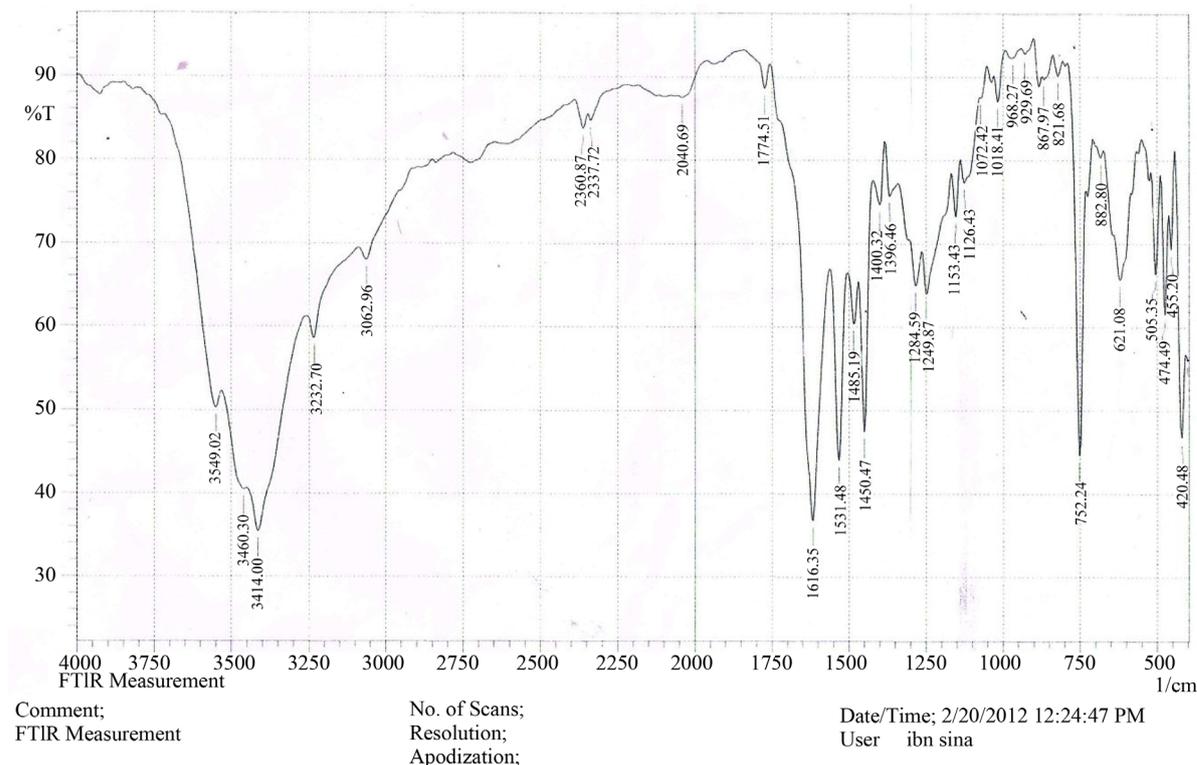
Purity of the obtained compound was examined by TLC, using chloroform and ethyl acetate (1:1) as effluent. The product color was brown yellow and the yield percentage was (83.76%) and the melting point was (70°C - 71°C). The reaction was clarified below:



The elemental analysis and some physical properties of the compound are in **Table 1**. The significant FTIR bands **Figure 1** of (Benzothiazol-2-ylamino) (2-hydroxy-phenyl)-acetonitrile compound and its assignments are

Table 1. Some physical properties and elemental analysis of 2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile.

Empirical Formula Mwt	Color	M.P. °C	Yield %	Elemental Analysis Calculated (Found)			
				C%	H%	N%	S%
C ₁₅ H ₁₁ N ₃ SO 281	yellow orange	70 - 71	83.76	64.06 (63.87)	3.91 (3.75)	14.95 (14.77)	11.39 (11.17)

**Figure 1.** FT-IR spectrum of 2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile.

given in **Table 2**. The FTIR showed some characteristic bands related to α -amino nitriles; like 2337 cm^{-1} which could be attributed to $\nu(\text{C}\equiv\text{N})$ group [32]. Infrared spectrum showed stretching band at 3233 cm^{-1} for $\nu(\text{N-H})$ band. The next characteristic band near 1616 cm^{-1} which could be attributed to $\delta(\text{N-H})$ group. The FTIR spectrum also showed a characteristic aromatic bands at 3062 cm^{-1} and out of plane bending at 752 cm^{-1} for ortho-substituted benzene ring, while it showed the disappearance of (C=O) band [33] [34]. The ^1H NMR spectra **Figure 2** of the same compound in DMSO with assignments are collected in **Table 3**. The ^1H NMR spectra showed besides the aromatic proton signals at 7 - 7.7 ppm, the phenolic OH proton has a signal 5.6 ppm the signals due to NH and CH appear at 3.4 and 4.8 ppm, respectively [35] [36]. ^{13}C NMR spectrum **Figure 3** shows result which was listed in **Table 4**.

3.2. Effect of Inhibitor Concentration

Figures 4(a)-(d) show the polarization curves for carbon steel in 3.5% NaCl in present and absent of different inhibitor concentration ranging between (10 - 1000) ppm, in temperature range (298 - 323) K. Electrochemical parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c and b_a) and corrosion current density (i_{corr}) were extracted by Tafel extrapolating the anodic and cathodic lines and are listed in **Table 5**.

The degree of surface coverage (θ) and the percentage of protection efficiency (P%) were calculated using the following equations [23] [26]:

$$\theta = i_{\text{ocorr}} - i_{\text{corr}} / i_{\text{ocorr}} \quad (4)$$

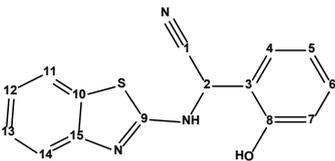
Table 2. The characteristic bands of FTIR spectra of Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile in (cm⁻¹).

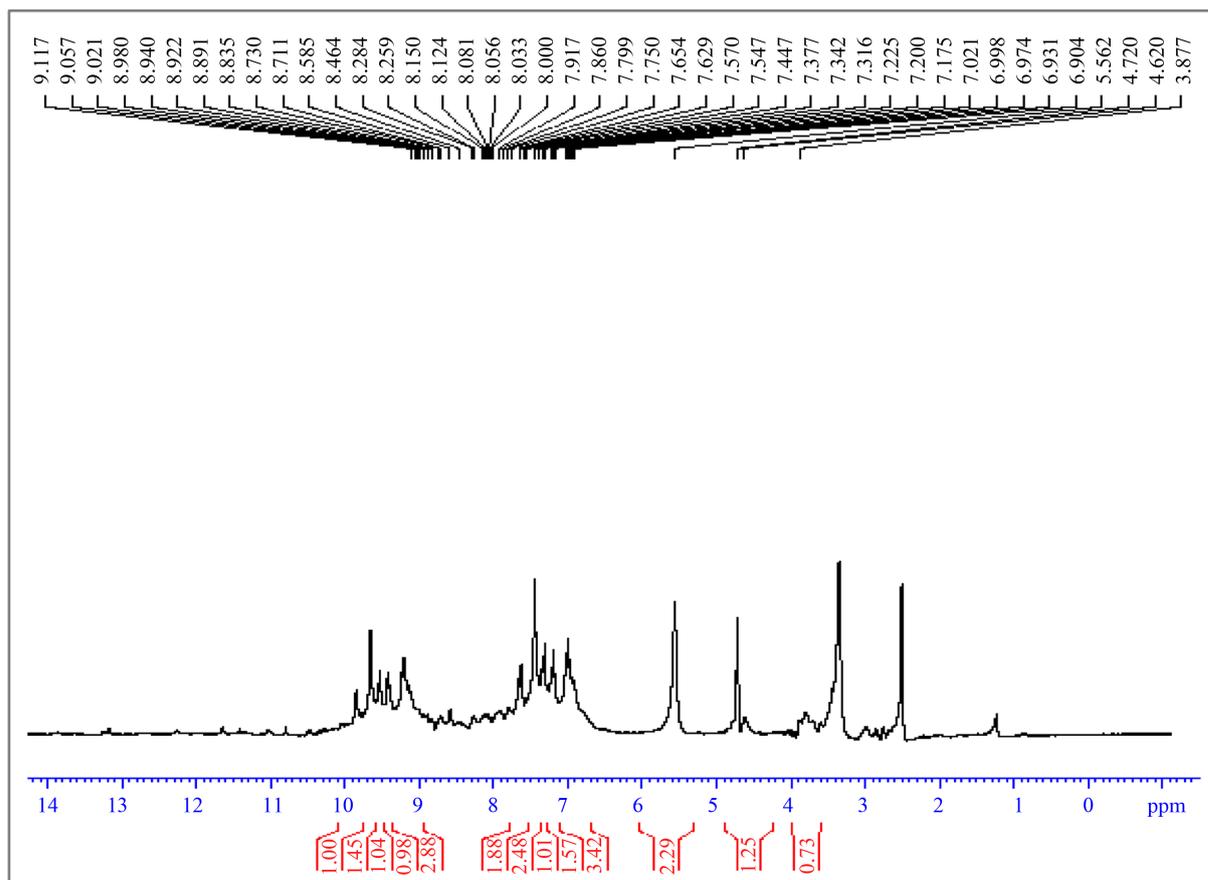
C ₁₅ H ₁₁ N ₃ SO	ν O-H cm ⁻¹	ν N-H cm ⁻¹	ν C-H cm ⁻¹ Aliphatic	ν C-H cm ⁻¹ Aromatic	δ C-H cm ⁻¹ Aromatic	ν C≡N Nitrile	δ N-H
	3414	3233	2970	3062	752	2237	1616

Table 3. ¹H NMR data for the 2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile in DMSO solution (ppm) δ -H.

C ₁₅ H ₁₁ N ₃ SO	Aromatic Protons	Phenolic OH Proton	NH Proton	CH Proton
	7.0 - 7.7	5.6	3.4	4.8

Table 4. ¹³C NMR data for 2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile.

Structure	¹ C	² C	⁸ C	⁹ C	C of All Aromatic
	117.5	56.5	155.5	168.5	120 - 130

**Figure 2.** ¹H-NMR spectrum of 2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile.

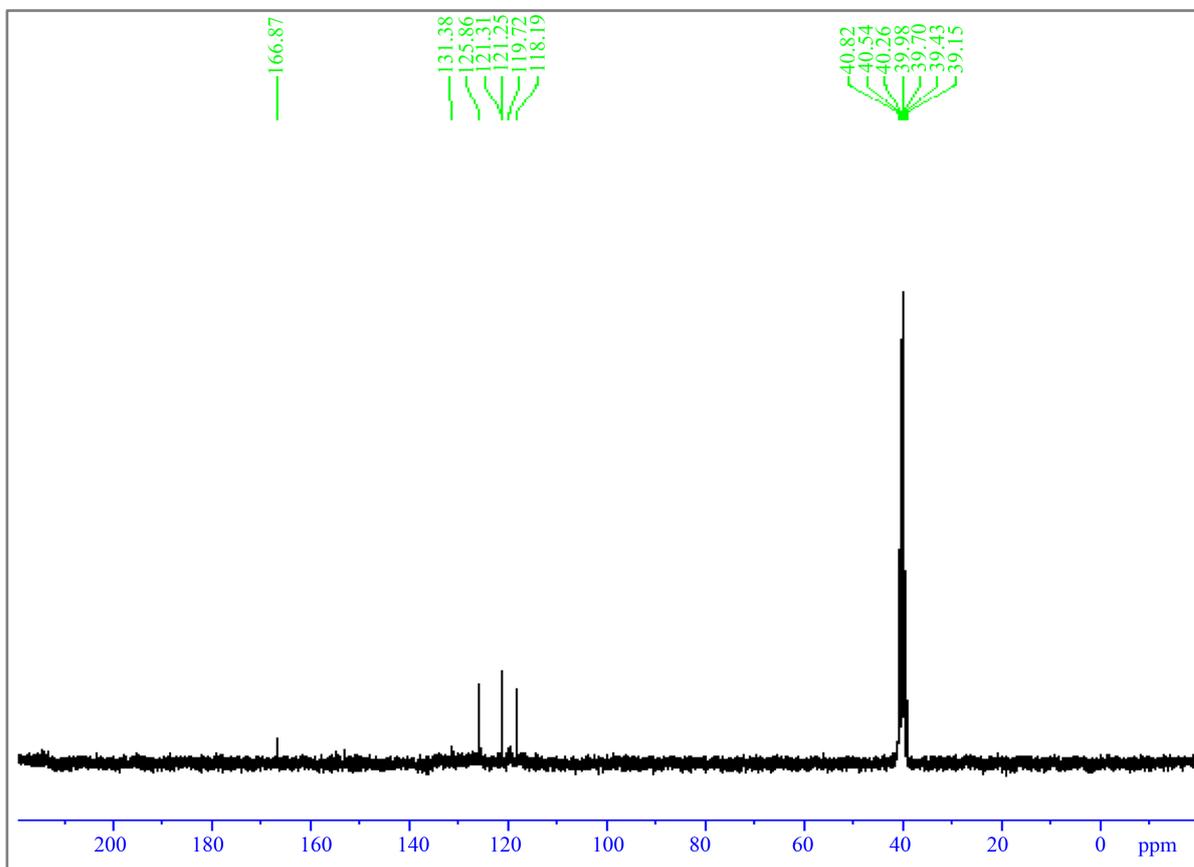


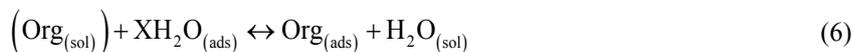
Figure 3. ^{13}C -NMR spectrum of 2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile.

$$P\% = \theta \times 100 \quad (5)$$

where i_{ocorr} and i_{corr} are corrosion current densities in the absent and present of inhibitor, respectively. From the result in **Table 1**, it can be observed that the values of corrosion current density (i_{corr}) of carbon steel in the inhibitor-containing solutions were lower than those for the inhibitor-free solution. The corrosion current densities at all inhibitor concentration are decreased.

3.3. Adsorption Isotherms

Adsorption isotherms provide information about the interaction of the adsorption molecules with the electrode surface [28]. The adsorption of an organic adsorbate at metal-solution interface can be presented as substitution adsorption process between the organic molecules in aqueous solution, ($\text{Org}_{(\text{sol})}$), and the water molecules on metallic surface, ($\text{H}_2\text{O}_{(\text{ads})}$) [25].



($\text{Org}_{(\text{sol})}$) and $\text{Org}_{(\text{ads})}$ are organic species dissolved in the aqueous solution and adsorbed onto the metallic surface, respectively, $\text{H}_2\text{O}_{(\text{ads})}$ is the water molecule adsorbed on the metallic surface and X is the size ratio respectively, the number of water molecules replaced by one organic adsorbate. For the studied inhibitor, it was found that the experimental data obtained from polarization reading could be fitted by Langmuir isotherm and Frumkin's isotherm. Among the two isotherms, the best fit adsorption isotherm is the Frumkin adsorption isotherm for adsorption of inhibitor on carbon steel surface with the mean R^2 value 0.9989. This means that there is an adsorption on a homogenous surface with interaction in the adsorption layer and the negative "a" value suggested that there is a decrease in the adsorption energy that is caused by the repulsive lateral force between the molecules in the adsorbed layer. The inhibitor follows Frumkin adsorption isotherm. The adsorption on a

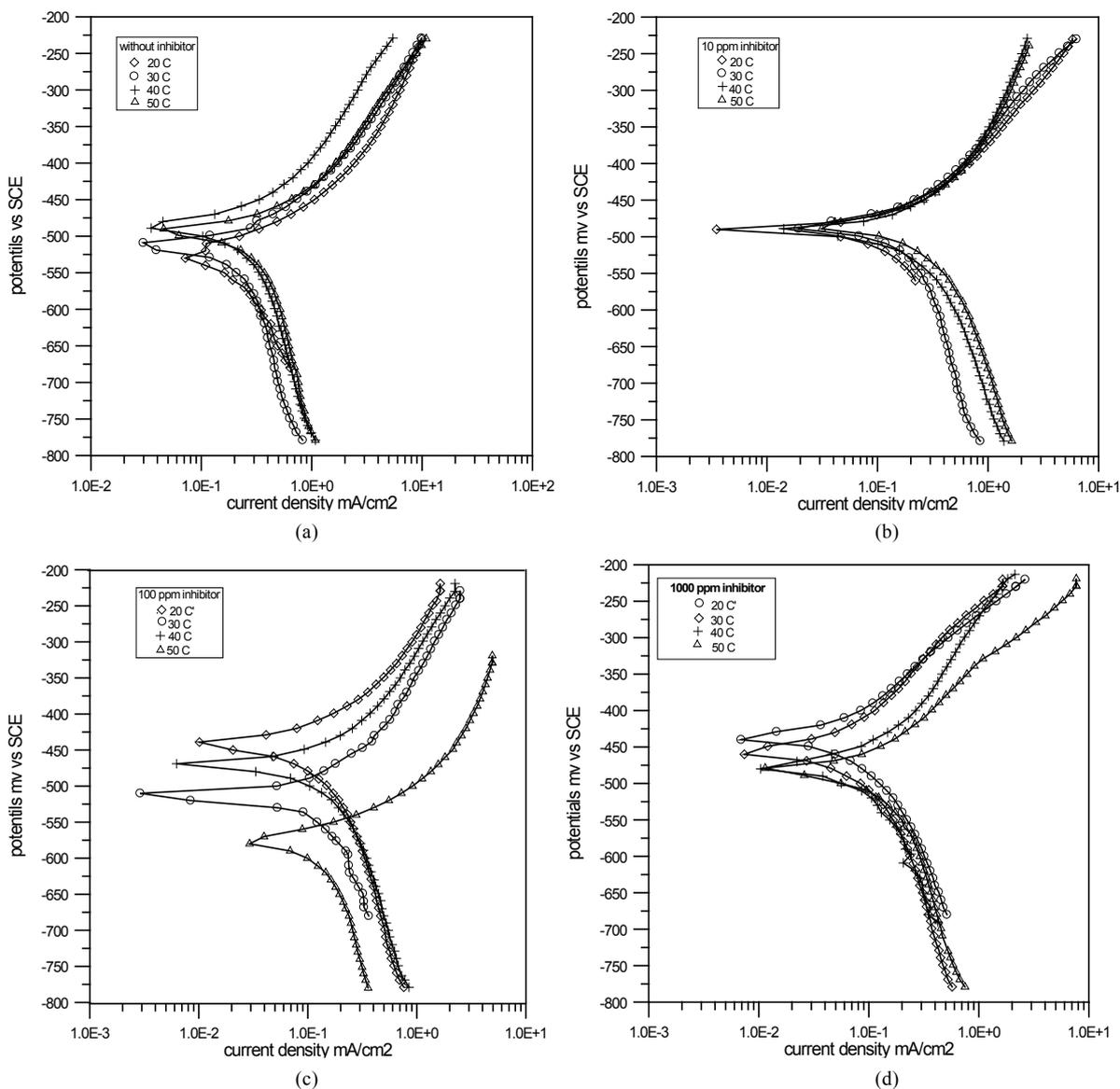


Figure 4. Tafel plots of carbon steel in 3.5% NaCl: (a) without inhibitor; (b) 10 ppm; (c) 100 ppm; (d) 1000 ppm at different temperatures.

homogenous surface with an interaction in the adsorption layer obeys Frumkin's isotherm [26].

The equation of Frumkin isotherm is;

$$\left\{ \frac{\theta}{(1-\theta)} \right\} e^{-2a\theta} = KC \quad (7)$$

Taking log on the both sides, it becomes;

$$\log \left\{ \frac{\theta}{(1-\theta)} C \right\} = \log K + 2a\theta \quad (8)$$

where "a" is the interaction parameter which can be positive or negative. A positive value indicates that the adsorption energy is increased by the lateral attraction between the adsorbed molecules and the negative values suggest that there is the presence of the lateral force of repulsion between the molecules in the adsorbed layer. Therefore, inhibitor after adsorption through N, O, S, atoms on the metal surface experiences lateral repulsive interactions among the N, CN, OH, S=. This also supplements that the adsorption of this inhibitor occurs via donation of electrons of N, O, S atoms to the metal.

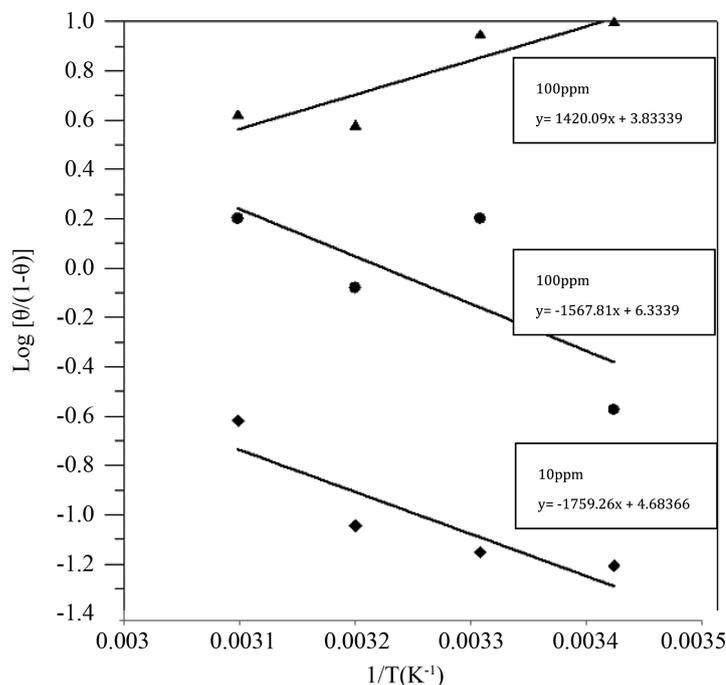


Figure 5. $\log[\theta/(1-\theta)]$ against $1/T$ plots of carbon steel in sea water without and with different concentration of the prepared inhibitor.

From **Figure 5** values of K and “ a ” are calculated from intercept and slope, respectively. The value of free energy of adsorption (ΔG_{ads}) are calculated by using the following equation [37].

$$\Delta G_{ads} = -RT \ln 55.5K \quad (9)$$

The various values are tabulated in the **Table 5**. The mean value of ΔG_{ads} for this isotherm is -34.2595 kJ/mol. The negative value of ΔG_{ads} indicates the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface. The low ΔG_{ads} value in the present case further confirms physical adsorption. Gibbs free energy values, ΔG_{ads} between -49 kJ/mol and -58 kJ/mol are indicative of chemisorption to Bereket *et al.* [38]. The low ΔG_{ads} value in the present case further confirms physical adsorption.

3.4. Effect of Temperature

The data in **Table 7** reveal the effect of temperature on i_{corr} and WL ($\text{g}/\text{m}^2\cdot\text{d}$), CR (mm/y), and P% for carbon steel in 3.5% NaCl solution. The result suggests that the inhibitor slightly adsorbed on carbon steel surface at all temperatures studied. The value of P% of different inhibitor concentration generally decreases with the increase of temperature. The apparent activation energy (Ea^*) for the corrosion process in absence and presence of the inhibitor was evaluated from Arrhenius equation [28]:

$$\log R_{corr} = \log A - Ea^*/2.303RT \quad (10)$$

where R_{corr} is the corrosion rate A is the frequency factor and Ea^* is the apparent activation energy, R is universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

The plot of logarithm of corrosion rate of carbon steel obtained from corrosion current densities versus the reciprocal of absolute temperature rang (293 - 323) K, give straight lines with slope of $-Ea^*/2.303RT$ as shown in **Figure 6**.

The thermodynamic parameters of carbon steel in 3.5% NaCl media in absence and in presence of inhibitor under test are given and they can be calculated using transition state Equation (11) [39].

$$CR_r = RT/Nh e^{\Delta S^*/R} \cdot e^{\Delta H^*/RT} \quad (11)$$

where CR is the corrosion rate, Ea is the apparent activation energy, R is the universal gas constant (8.314

Table 5. Equilibrium constant and Gibbs free energy values for the inhibitor at various temperatures calculated from Frumkin isotherm.

Temp	<i>a</i>	<i>K</i>	<i>R</i> ²	$\Delta G_{ad}/\text{kJ}\cdot\text{mol}^{-1}$
293	-0.972	27.352	0.9988	-34.671
303	-0.996	6.8077	1.0000	-14.950
313	-1.7305	92.683	0.9967	-40.161
323	-2.328	790.678	0.9999	-47.256

Table 6. Polarization measurements summary of carbon steel specimens in artificial sea water (3.5% NaCl)/inhibitor at different temperatures.

System (3.5% NaCl)	Temp. °C	E _{corr} mv vs. SCE	<i>i</i> _{corr} μA/cm ²	<i>a</i> mV/Dec	<i>b</i> mV/Dec	WL g/m ² ·d	CR mm/y	P%	θ
Without Inhibitor	293	-526	126	168	80	31.6	1.47	-	-
=	303	-512	143	213	90	36.0	1.65	-	-
=	313	-489	150	177	109	37.6	1.75	-	-
=	323	-497	204	214	96	51.0	2.37	-	-
10 ppm Inhibitor	293	-563	97	171	101	24.5	1.14	23.01	0.23
=	303	-484	108	189	109	36.0	1.26	24.47	0.24
=	313	-489	110	144	108	27.6	1.28	26.66	0.26
=	323	-468	132	135	117	33.0	1.53	35.29	0.35
100 ppm Inhibitor	293	-440	55	143	85	13.8	0.64	56.34	0.36
=	303	-510	64	141	92	16.0	0.63	55.24	0.55
=	313	-469	78	162	100	19.6	0.90	48.00	0.48
=	323	-578	90	203	78	22.5	1.04	55.88	0.55
1000 ppm Inhibitor	293	-455	34	120	112	8.57	0.40	73.01	0.73
=	303	-439	40	124	115	10.0	0.46	72.02	0.72
=	313	-474	54	167	104	13.5	0.63	64.00	0.64
=	323	-476	72	175	101	18.1	0.84	64.78	0.65

$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), *T* is temperature, *A* is the Arrhenius pre-exponential factor, *h* is the Plank's constant ($6.626176 \times 1034 \text{ J}\cdot\text{s}$), *N* is the Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. The values of Ea^* , ΔH^* and ΔS^* were calculated as shown in **Figure 7** which represents the plot of $\log(CR_p/T)$ against $(1/T)$.

Straight lines are obtained with a slope of $(-\Delta H^*/2.303R)$ and an intercept of $(\log R/Nh + \Delta S^*/2.303R)$ from which the values of ΔH^* and ΔS^* were calculated. Then ΔG^* calculated using the following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (12)$$

and listed in **Table 7**.

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation in absence and in presence of the inhibitors give some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature, with analogous increase in corrosion activation energy in the presence of (100, 1000) ppm compared to its absence, is frequently interpreted as being suggestive of a physical adsorption [40].

Also the lower ΔH^* values indicate that the inhibited corrosion reaction of carbon steel is supporting the proposed physisorption mechanism [34] [41]. The entropy of activation ΔS^* in the presence inhibitor is small and negative values. This implies that the activated complex in the rate determining step represents dissociation rather

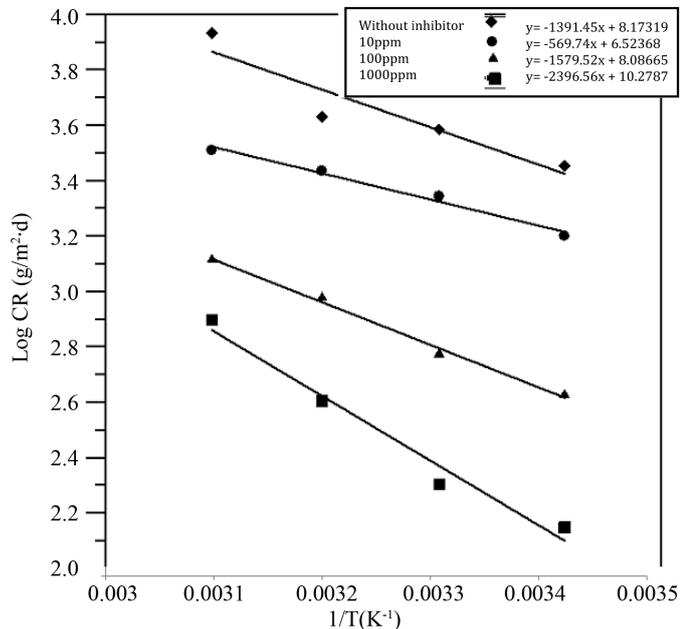


Figure 6. Arrhenius plots of carbon steel in sea water without and with different concentration of the prepared inhibitor.

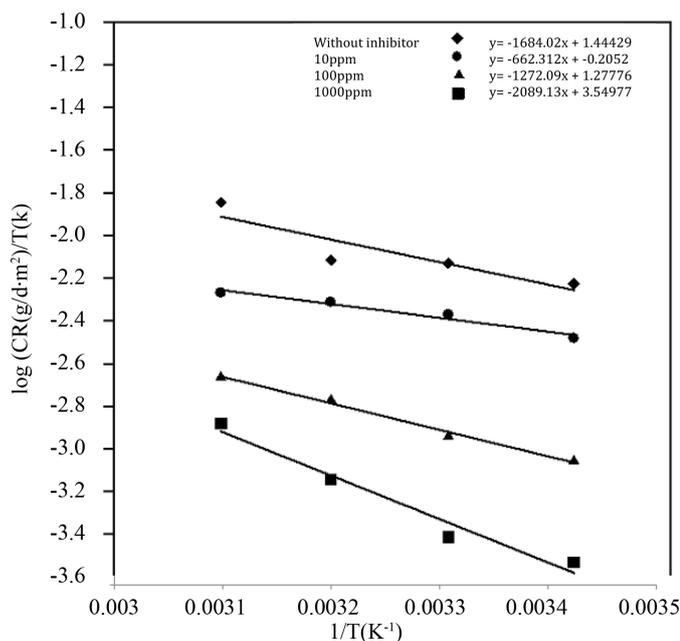


Figure 7. $\log[CR(g/d.m-2)/T(K-1)]$ against $1/T(K-1)$ plots of carbon steel in sea water without and with different concentration of the prepared inhibitor.

than association meaning that the increase in a disordering takes place on going from activated complex to reactants, which ΔS^* values in absence of inhibitor is more small and negative that indicate to the association rather than of presence inhibitor [41].

The activation energy for corrosion reaction with using 10 ppm inhibitor was lower than in absence of inhibitor, that indicate the increasing in the ability of the corrosion rate a cording to uncompleted adsorption layer but log A values decreased with adding low inhibitor concentration.

Table 7. The values of activation parameters Ea^* , ΔH^* , ΔS^* , and ΔG^* for carbon steel in 3.5% NaCl in absence and presence of different inhibitor concentration (10, 100, 1000) ppm.

Inhibitor Conc.	Ea^* kJ·mol ⁻¹	ΔH^* kJ·mol ⁻¹	ΔS^* / J·mol ⁻¹ ·K ⁻¹	$\Delta G^*/\text{kJ}\cdot\text{mol}^{-1}$			
				20 C	30 C	40 C	50 C
0	11.660	19.8713	-252.70	93.60	96.15	98.67	101.20
10	7.3850	4.8253	-305.30	93.94	97.15	100.35	103.56
100	13.192	10.6306	-290.18	95.60	98.50	101.40	104.30
1000	20.018	17.4576	-271.20	96.56	99.26	101.96	104.66

4. Conclusion

2-(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile was prepared and identified successfully, then used as corrosion inhibitor. The value of i_{corr} in case of presence of inhibitor in the three concentrations was lower than i_{corr} in absence of inhibitor. A best protection efficiency was 73.01% in the case using 1000 ppm of the inhibitor at 293 K, and by increasing temperature, protection efficiency decreased in general; the kinetics and thermodynamic study showed that the inhibitive action took place through the physisorption of the inhibitor molecules on the carbon steel surface and that the adsorption of inhibitor on carbon steel surface obeyed Frumkin isotherm.

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