Synthesis and characterization of some 2-sulphanyl benzimidazole derivatives and study of effect as corrosion inhibitors for carbon steel in sulfuric acid solution

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Abstract

This research involves the synthesis of some sulphanyl benzimidazole derivatives (Ia-c), which were prepared from reaction of 2-mercaptobenzimidazole substituted benzyl halide, and structures were identified by spectral methods[FTIR, ^{1}H-NMR and ^{13}C-NMR].These compounds were investigated as corrosion inhibitors for carbon steel in 1M H_2SO_4 solution using weight loss, potentiostatic polarization methods; obtained results showed that the sulphanyl benzimidazole derivatives retard both cathodic and anodic reactions in acidic media, by virtue of adsorption on the carbon steel surface. This adsorption obeyed Langmuir's adsorption isotherm. The inhibition efficiency of (Ia-c) ranging between (65-92) %. By using different Ib derivative concentration and temperature, the carbon steel corrosion rate was decreased with increasing Ib concentration and the highest inhibition efficiency reach to 92.8% by using 4.6×10^{-4} M Ib concentration at 308 K,the inhibition efficiency increases with increasing temperature ranging(308-338)K.

Keywords: benzimidazole derivatives,carbon steel,acid inhibition,polarization

تحضير وتشخيص بعض مشتقات السلفانيل بنزايميدازول ودراسة تأثيرها كمثبطات تآكل لحديد الفولاذ في محلول حامض الكبريتيك

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الخلاصة:

يتضمن البحث تحضير بعض مشتقات السلفانيل بنزايميدازول (c–aI)، حضرت من تفاعل 2– مركبتوبنزايميدازول مع هاليدات البنزايل المعوضة، وتم تشخيص التراكيب بواسطة الطرائق الطيفية (الأشعة تحت الحمراء والرنين النووي المغناطيسي لل ^{1}H، ^{13}C) وقياس بعض الثوابت الفيزياوية .تمت دراسة تأثير المركبات المحضرة كمثبطات لتآكل حديد الفولاذ في محيط 1 مولاري حامض الكبريتيك باستخدام طريقتي فرق الوزن وقياس منحني الاستقطاب بالمجهاد الساكن. بينت النتائج ان مشتقات السلفانيل بنزايميدازول المحضرة قللت من سرعة التفاعل الانودي والكاثودي على حدّ سواء في المحيط الحامضي وان هذه الاعاقة ناتجة عن أمتزازها على سطح الفولاذ.وعملية الأمتزاز كانت تطيع متساويات الحرارة من نوع لانكماير.وصلت نسبة كفاءة التثبيط للسطح باستخدام المشتقات الثلاثة (65–92)% .تمت دراسة تأثير تراكيز مختلفة من المشتق Ib ودرجات حرارة مختلفة وتبين ان زيادة تركيزه تؤدي الى زيادة كفاءة التثبيط ووصلت أعلى نسبة 92.8 % عند استخدام $10^{-4}\times 4.6$ مولاري عند درجة 308 كلفن وتزداد كفاءة التثبيط بزيادة درجات الحرارة (308–338) كلفن.

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1. Introduction

Carbon steel has been extensively used under different conditions in petroleum industries [1]. Acid solutions were widely used for industrial cleaning of boilers, descaling and oil well acidification and in the petrochemical processes [2]. Acids are generally used in the pickling processes of metals and alloys [3,4]. Mostly, sulfuric and hydrochloric acids are employed for such purposes [5].The main problem concerning carbon steel applications is its relatively low corrosion resistance in acidic solutions. Several methods are currently used to prevent corrosion of carbon steel. One such method is the use of an organic inhibitor [6-8]. Heterocyclic organic compounds containing π bonds, heteroatom phosphorus, sulfur, nitrogen and oxygen are often used for this purpose [9-14].The inhibition efficiency should follows the sequence $O < N < S < P$ [15]. Generally, N-containing inhibitor functions more efficiently in HCl, while S-containing inhibitor in H_2SO_4 [16]. Furthermore, the compounds containing both nitrogen and sulfur can provide excellent inhibition, compared with compounds containing only nitrogen or sulfur [17].Study of organic corrosion inhibitors is an attractive field of research due to its usefulness in various industries [18]. Among these,benzimidazole and its derivatives intensively were investigated as effective corrosion inhibitors in various acid solutions [19-23]. The organic inhibitors function through adsorption on metal surface blocking the active sites by displacing water molecules and forming a compact barrier film to decrease the corrosion rate [24,25]. The adsorption of these molecules depends mainly on certain physicochemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and π orbital character of donating electrons and the electronic structure of the molecules [26-28]. Adsorption can be described by two main types of interaction as follows, (a) Physical adsorption, 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[29], (b) Chemical adsorption, 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 [30]. Chemical adsorption is typified by much stronger adsorption energy than physical adsorption. Such a bond is therefore more stable at higher temperatures. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, temperature, the presence of dissolved inorganic and/or organic substances even in minor amounts and, of course, on the type of metallic material supposed to be protected [31]. Benzimidazole molecule shows two anchoring sites suitable for surface bonding: the nitrogen atom with its lonely sp^2 electron pair and the aromatic rings [23,32].

The purpose of this paper is to synthesis of some sulphanyl benzimidazole derivatives and characterized by using [FTIR, ^{1}H-NMR and ^{13}C-NMR].; then evaluated as corrosion inhibitors for carbon steel in 1M H_2SO_4 solution by using potentiostatic and weight loss measurements. The adsorption and inhibition efficiency of these inhibitors were also investigated.

2. Experimental

Instruments

Melting points were measured with a Gallen Kamp melting point apparatus. The FTIR-spectra of compounds were recorded on a Shimadzu FTIR-8300 spectrophotometer as KBr disc, results are given cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker spectro Spin ultra-shield magnets 300 MHz instrument, using DMSO-d^6 as solvent and TMS as internal reference [Al al-Bayt University, Jordan] . The carbon steel was analyzed by using Spectro max$_x$ device (Germany). The Weight loss were measured with Sartorius Ag Gottigen BL210S (Germany) Electronic precision balances and preions metal scales with capacities ranging 0.1mg to 12kg.

Polarization measurements were conducted with the use of advanced potentiostat winking MLab-200(2007)[Bank Elektronik-Intelligent controls GmbH with all accessories], A cell containing three compartments for electrodes was used. The working polished carbon steel electrode with exposed area 1 cm^2 was dipped in the test solution. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and the counter electrodes, respectively (Germany). All potentials were measured *vs*. SCE.

Chemical

Starting chemical compound was obtained from Fluka and Aldrich or BDH.

Synthesis of 2-alkyl sulphanyl -1*H*-benzimidazole derivatives (Ia-c)

2-mercaptobenzimidazole **I** was synthesized according to reported procedure [33].2-mercaptobenzimidazole **I** (1.502 g, 0.01 mole) was dissolved in absolut ethanol (35 ml) was added to a solution of potassium hydroxide (0.5611 g, 0.01 mole) in absolut ethanol (15 ml).After 15 min of stirring at room temperature, substituted benzyl halide **(**0.01mole) was added in 2–3 portions, and the resultant suspension was reflux with stirring for 3-4 hrs. The reaction mixture was cooled and poured into ice bath with stirring a white solid was precipitated and left for overnight. The solid was filtered off, washed with cold water and air-dried. The crude products were purified by recrystalization from ethanol, to afford white needles of the pure compounds **(Ia-c)**.Physical properties of the dry products are listed in Table-1.

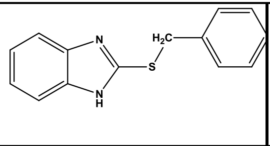
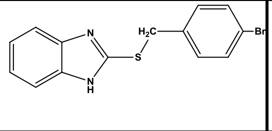
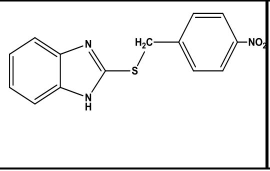
Specimen

Carbon steel specimens with composition 0.086% C, 0.252%Mn, 0.003%P, 0.016% S and the remainder being Fe were used. Specimens of size 2cm x 1cm x 0.2cm were used for the weight loss and of 1.5cm diameter specimen were used for polarization method**.** These samples were polished successively with (i) belt grinding polishing machine, (ii) polished with emery papers of different grit (80, 150, 220, 240, 320, 400, 1000, 1200 and 2000) in sequence. After polishing the specimens were washed with distilled water then acetone finally dried and kept in desiccator.

Weight loss method

The specimens for weight loss measurements were polished with emery paper (80, 150, 220, 240, 320, 400, 1000, 1200 and 2000) in sequence. Each run was carried out in a glass vessel containing 75 ml test solution.A clean weighed carbon steel specimen was completely immersed at an inclined position in the vessel. After a period of time up to 5 hours at 303±1 K of immersion in 1M H_2SO_4 with and without addition of inhibitor(Ia-c), the specimen was withdrawn, rinsed with distilled water, washed with acetone, dried and weighted using an analytical balance. The average weight loss for each two identical experiments was taken and expressed in ($g/m^2.d$)

Table 1-Physical properties and FTIR spectral of compounds (Ia-c)

Comp. No.	Comp. structure	Melting point °C	Yield %	color	Major FTIR Absorptions cm^{-1}				
					νN-H	νC-H arom.	νC-H aliph.	νC=N	Other bands
Ia		189-190	80	White	3182	3058	2956	1652	ν mono-sub. 709,744
Ib		205-206	88	White	3192	3072	2958 2879	1598	νC-Br 669 νp-position 823
Ic		193-195	84	White	3185	3076	2952 2873	1615	ν$N=O_2$ Asym.1517; sym.1348 νpara-position 852

Potentiostatic polarization study

The electrochemical measurements were performed in a typical three-compartment glass cell consisted of the carbon steel specimen as working electrode (WE), platinum counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode. The reference electrode was connected to a Luggin capillary to minimize IR drop. Solutions were prepared by diluted H_2SO_4 with distilled water, the carbon steel electrode was abraded with different grit emery papers , cleaned with acetone, washed with distilled water and finally dried. The electrode potential was allowed to stabilize 15 min before starting the measurements.Tafel polarization curves were obtained by changing the electrode potential automatically from -200 mV versus open circuit potential(OCP) to +200mV versus OCP with scan rate of 2.0 mV s^{-1}. All experiments were conducted at 308 ±1 k for different inhibitor (Ia-c) at 3.5×10^{-4} M. Different concentration (1.5×10^{-4}, 3.5×10^{-4} , 4.6×10^{-4})M at 308-338 k were examined .Tafel lines of potential versus log (I) were plotted and corrosion current density(I_{corr}) and corrosion potential (E_{corr}) were determined in the absence and presence of inhibitor.

3. Results and discussion

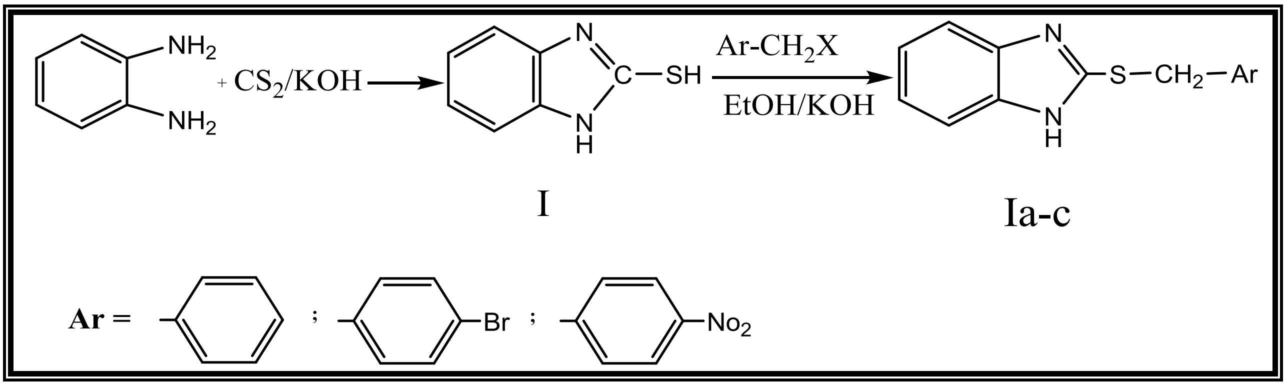
(i) corrosion inhibitor synthesis

Most of the heterocyclic compounds are very important organic compound having wide spectrum of corrosion inhibitors of carbon steel in acid media. The initial mechanism in any corrosion inhibition process is the adsorption of the inhibitor on the metal surface can be facilitated by the presence of hetro atoms such as (N,O,P and S) [10,25]. A new organic compounds containing (N and S) atoms prepared for used as a corrosion inhibitors. The synthesis some of new sulphanyl benzimidazole derivatives (Ia-c) show in scheme (1).

Compound (I) was prepared according to the literatures [33].The route include synthesis of 2-(alkyl) sulphanyl-1*H*-Benzimidazole derivatives (Ia-c), by condensation of the 2-mercaptobenzimidazole with substituted benzyl halide and potassium hydroxide in absolute ethanol media under reflux condition,and the end point of the reaction was examined by TLC.The structure of these compounds (Ia-c) were confirmed by physical properties are listed in Table 1. FT-IR spectra showing ν C-H aliph. In addition 605 for C-Br (Ib);1517 asym.,1348 sym. For νNO_2 group (Ic).While the ^{1}H-NMR spectra data of compounds (Ia-c) [34] δ ppm in DMSO-d^{6} solvent are listed in Table 2.

4.51-4.7 [S,2H,-S-CH_2]; 7.2-7.8 [m,9or8H,Ar-H]; 12.3-12.4 [S,1H,NH imidazole].

^{13}C-NMR spectra show result were listed in Table 3. Other chemical test was carried out characterize the prepared Ib and Ic such as sodium fusion and Tollene's reagent for bromine and –NO_2 group tests respectively [35].



Scheme 1- 2-(alkyl) sulphanyl -1*H*- Benzimidazole derivatives (Ia-c)

Table 2-^{1}H-NMR spectral data(ppm) for some of the prepared compounds (Ia-c)

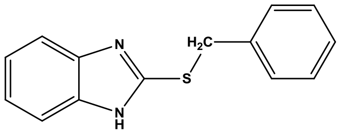
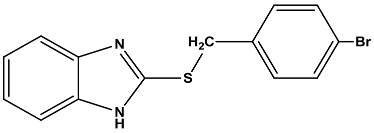
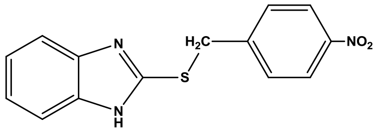
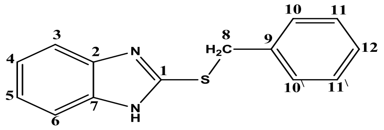
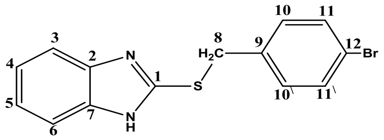
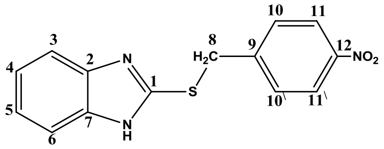
Comp. No.	**Compound structure**	**^{1}H-NMR parameters (ppm) δ-H**
Ia		4.54(s,2H,-S-CH_2-);7.11-7.48(m,9H,Ar-H); 12.55(s,1H,NHimidazole)
Ib		4.54(s,2H,-S-CH_2-);7.11-7.51(m,8H,Ar-H); 12.55(s,1H,NHimidazole)
Ic		4.51(s,2H,-S-CH_2-);7.21-7.82(m,8H,Ar-H); 12.52(s,1H,NHimidazole)

Table 3- ^{13}C-NMR spectral data for some of the prepared compounds(Ia-c)

Comp. No.	Compound structure	^{13}C-NMR data (ppm)
Ia		61.07(C^8);110-122(C^3,C^4,C^5,C^6,$C^{10,10\backslash}$,$C^{11,11\backslash}$and C^{12}); 124.54(C^9);131.48(C^7);139.68(C^2);158.64(C^1)
Ib		62.0 (C^8);110-120(C^3,C^4,C^5,C^6,$C^{10,10\backslash}$,);121.13(C^9) 121.66 ($C^{11,11\backslash}$);130.99(C^{12}); 131.29(C^7);137.47(C^2); 149.34(C^1)
Ic		61.07(C^8);119-129(C^3,C^4,C^5,C^6,$C^{10,10\backslash}$and$C^{11,11\backslash}$); 130.01(C^9);134.97(C^2 and C^{12});135.59(C^7);160.53(C^1)

(ii)Weight loss measurements

The gravimetric measurements of carbon steel immersed in 1M H_2SO_4 in the absence and presence of different inhibitors of sulphanyl Benzimidazole derivatives (Ia-c) were investigated and determined after 5 hours of immersion time at 303 K, 3.5×10^{-4} M concentration of these inhibitors was chosen to compare the inhibition efficiency of the three compounds, weight loss of carbon steel samples are decreased in the present of the three compounds. This means that these compounds retards the corrosion of carbon steel in 1 M H_2SO_4 or in other words, these compounds act as inhibitors. The corrosion rate of carbon steel was determined using the relation:

$$R = \frac{\Delta m}{A * t} \qquad (1)$$

Where Δm is the mass loss (mg), A the area (cm^2) and t immersion period (hour). The value of the percentage inhibition efficiency (% IE), and a parameter surface coverage (θ) which represents the part of the surface covered by the inhibitors molecules, for the corrosion of carbon steel was calculated as follows [36]:

$$\% IE = \frac{(R - R_{inh})}{R} \times 100 \qquad (2)$$

$$\theta = \frac{(R - R_{inh})}{R} \qquad (3)$$

Where R and R_{inh} are the uninhibited and the inhibited corrosion rate, respectively.The calculated values of corrosion rate ($g/m^2.d$), surface coverage (θ) and inhibition efficiency (% IE) at 308 k are given in Table 4.

According to this data, it is clear that using 3.5×10^{-4} M of sulphanyl Benzimidazole derivatives reduces the corrosion rate of carbon steel in sulfuric acid solution, the order of inhibition efficiency (% IE) of investigated sulphanyl benzimidazole derivatives is as follows:

Ib > Ic > Ia Which means that the inhibition efficiency depend on the substituent nature groups.

Table 4 - Data of corrosion rate, degree of surface coverage and inhibition efficiency for carbon steel in 1M H_2SO_4 solution in the absence and presence of 3.5×10^{-4} M of the three inhibitors at 303 K

inhibitor	R ($g/m^2.d$)	θ	% IE
blank	389.04	--	--
Ia	131.52	0.66	66.19
Ic	95.76	0.75	75.38
Ib	27.6	0.92	92.90

(iii)Polarization measurements

Potentiostatic polarization curves were plotted for the corrosion of carbon steel in 1M H_2SO_4 solution in the absence and presence of 3.5×10^{-4} M sulphanyl benzimidazole derivatives (Ia-c) at 308 k as shown in Figure 1.

A linear region with apparent Tafel was observed, the cathodic reaction was activation-controlled and the addition of the compounds tested decreased the current densities in large anodic and cathodic domains of potential. This result indicated that the compounds studied acted as mixed-type inhibitors. Generally, the addition of mixed inhibitors in solution does not change corrosion potential significantly because they inhibit both the anodic and cathodic reactions. Small changes in potentials can be a result of the competition of the anodic and the cathodic inhibiting reactions, and of the metal surface condition [37]. The values of various electrochemical parameters are summarized in Table 5. The value of the percentage inhibition efficiency (% IE), and a parameter surface coverage (θ) which represents the part of the surface covered by the inhibitors molecules, for the corrosion of carbon steel was calculated as follows [38]:

$$\%IE = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \qquad (4)$$

$$\theta = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \qquad (5)$$

Where I_{corr} and $I_{corr(inh)}$ are the corrosion currents densities in the absence and in presence of the inhibitor,respectively which determined by extrapolation of the cathodic and anodic Tafel lines to corrosion potential (E_{corr}).From Table 5, it was clearly seen that cathodic slope were found similar indicating that the reduction of hydrogen did not modified in the presence of the inhibitors tested. Thus, the presence 3.5×10^{-4} M of sulphanyl benzimidazole derivatives leads to decrease in the values of I_{corr} , which was particularly significant in the case of (Ib).

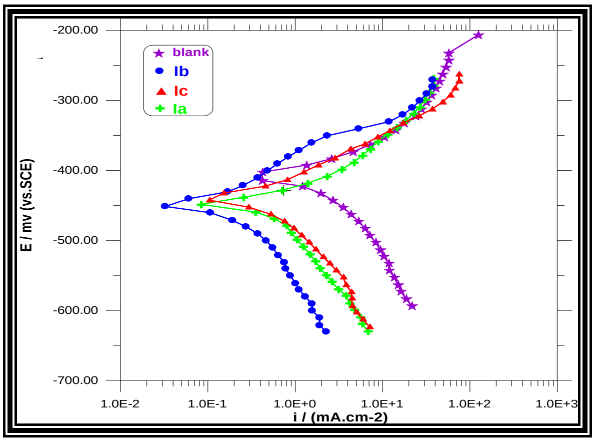


Figure 1- Polarization curves of carbon steel in 1M H_2SO_4 in the absence and presence of 3.5×10^{-4} M sulphanyl benzimidazole derivatives (Ia-c) at 308 K

Table 5 - polarization parameters of carbon steel in 1M H_2SO_4 in the absence and presence of 3.5×10^{-4} M sulphanyl benzimidazole derivatives (Ia-c) at 308 K

solution	E_{corr} Mv (SCE)	I_{corr} μA/cm^2	βc mV/dec	βa mV/dec	W.L g/m^2.d	Penetration loss mm/a	θ	% IE
Blank	-411.8	1450	-109.2	70.5	363	16.9	--	--
Ia	-449.9	504.14	-151.3	63.8	126	5.85	0.65	65.23
Ic	-439.9	316.91	-92.9	60.9	79.2	3.68	0.78	78.14
Ib	-452.2	110.78	-75.5	80.2	27.7	1.29	0.92	92.36

(iv) Effect of inhibitor (Ib) concentration

Effect of 2-(p-bromobenzyl) sulphanyl -1*H*-Benzimidazole (Ib) was investigated in the concentration range (1.5×10^{-4} – 4.6×10^{-4})M. Figure 2 shows the Tafel polarization value of carbon steel immersed in 1M H_2SO_4 at 308 k with and without (Ib)inhibitor.

polarization parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (βc and βa) and corrosion current density (I_{corr}) were extracted by extrapolating the anodic and cathodic branches of Tafel curves at potentials beyond the region of Ecorr ±30 mV, using Softcorr III program and are listed in Table 6.

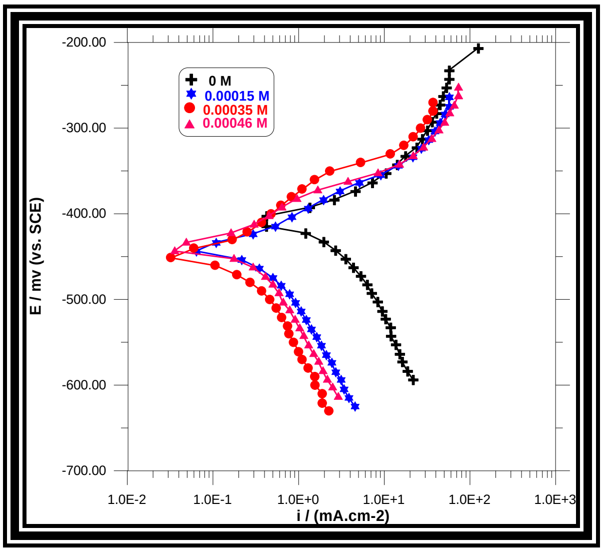


Figure 2- Polarization curves of carbon steel in 1M H_2SO_4 in the absence and presence of inhibitor (Ib) different concentration at 308 K

From the results collected in Table 6, it can be seen that by increasing the inhibitor concentration, the corrosion rate is decreased in acid media and inhibition efficiency increased as shown in Figure 3. Therefore, it can be concluded that they impede the corrosion by merely blocking the reaction sites on carbon steel surface without interfering the anodic and cathodic reactions. Moreover, this inhibitor cause no significant changes in the anodic and cathodic Tafel slopes, This suggest that this inhibitor behave as a mixed-type inhibitor. Indicating that the inhibitor can be classified as adsorptive-type [37].

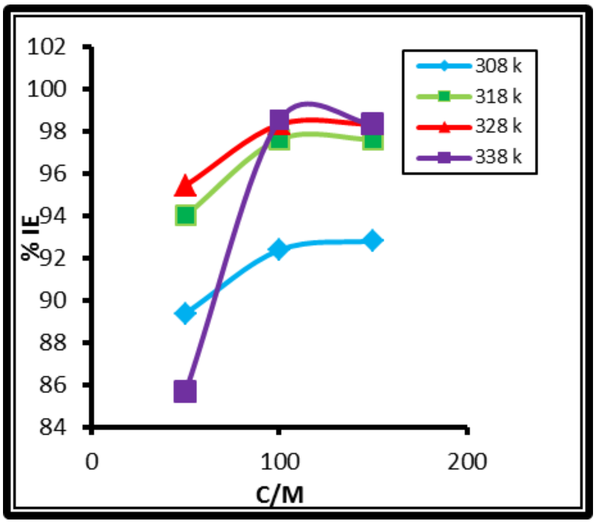


Figure 3- relationship between inhibition efficiencies and various concentrations from inhibitor(Ib) for carbon steel in 1M H_2SO_4

Table 6- polarization parameters of carbon steel in 1M H_2SO_4 in the absence and presence of different concentrations of (Ib) at 308 K

Inhibitor conc. (M)	E_{corr} mv (SCE)	I_{corr} $\mu A/cm^2$	βc mV/dec	βa mV/dec	W.L $g/m^2.d$	Penetration loss mm/a	θ	% IE
0	-411.8	1450	-109.2	70.5	363	16.9	--	--
1.5×10^{-4}	-442.7	154.26	-65.6	52.5	38.6	1.79	0.89	89.36
3.5×10^{-4}	-452.2	110.78	-75.5	80.2	27.7	1.29	0.92	92.36
4.6×10^{-4}	-435.6	104.31	-66.8	53.6	26.1	1.21	0.92	92.80

(v)Adsorption isotherms

Basic information on the interaction between inhibitors and metal surface can be provided using the adsorption isotherms [39].The adsorption of an organic adsorbate at metal–solution interface can occur as a result of substitutional adsorption process between organic molecules presented in the aqueous solution ($Org_{(sol)}$), and the water molecules previously adsorbed on the metallic surface ($H_2O_{(ads)}$) [40]:

$$Org_{(sol)} + xH_2O_{(ads)} = Org_{(ads)} + xH_2O_{(sol)} \qquad (6)$$

where $Org_{(sol)}$ and $Org_{(ads)}$ are the organic species in the bulk solution and adsorbed one on the metallic surface, respectively,$H_2O_{(ads)}$ is the water molecule adsorbed on the metallic surface and x is the size ratio representing the number of water molecules replaced by one organic adsorbate. In order to obtain the adsorption isotherm, the degree of surface coverage, θ, for different concentrations of inhibitor in 1M H_2SO_4 solution has been evaluated by equation (5).

The θ values are presented in Table 7. According to the Langmuir's isotherm, the surface coverage (θ) is related to inhibitor concentration (C) by the following equation [41]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (7)$$

Where K_{ads} is the equilibrium constant of the inhibitor adsorption process. A straight line is obtained on plotting C/θ versus C as shown in Figure 4. The linear correlation coefficient (r^2) is almost equal to 1 ($r^2 = 0.9999$)
and the slope is very close to 1, indicating the adsorption of synthesized inhibitor(Ib) on the carbon steel surface obeys the Langmuir adsorption isotherm.

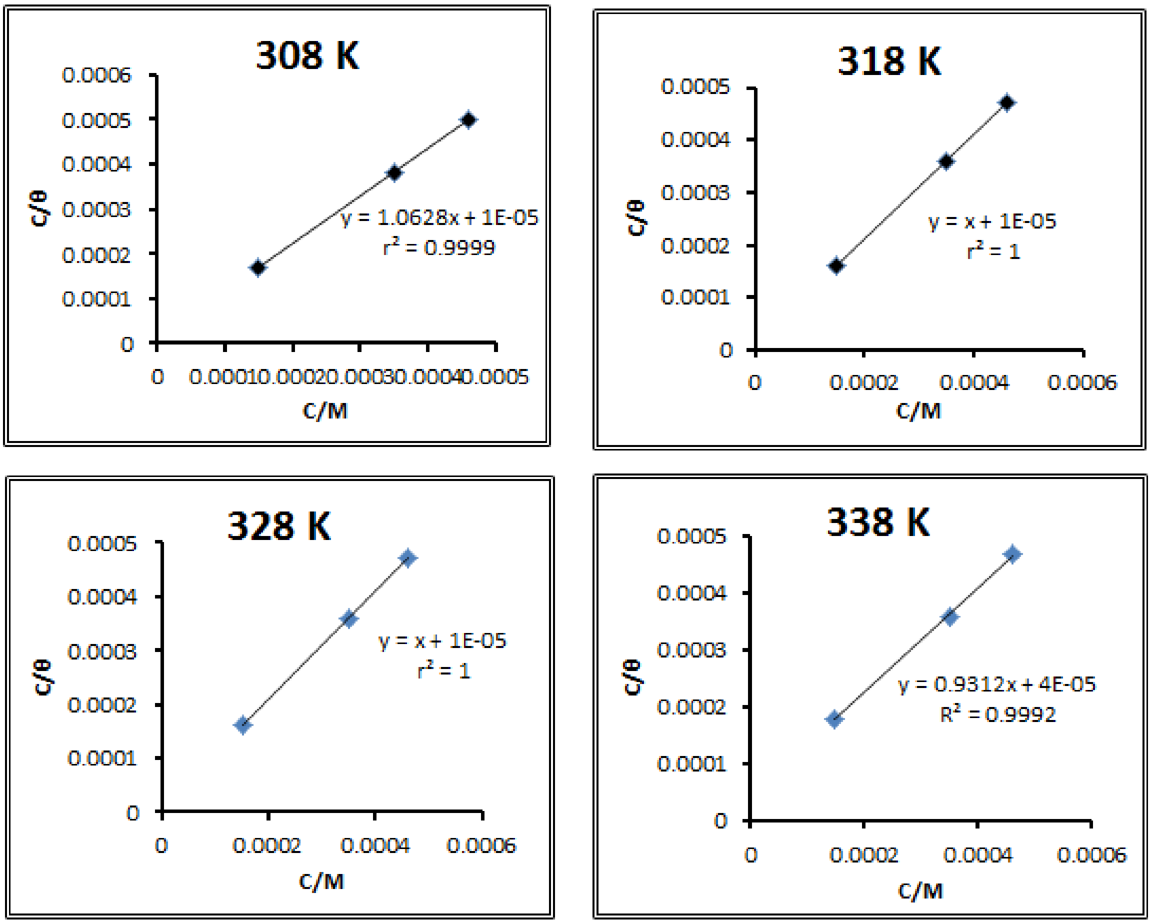


Figure 4-The Langmuir isotherm adsorption for carbon steel in 1M H_2SO_4 in the different concentrations of inhibitor (Ib) at (308-338) K

Table 7- Data of degree of surface coverage and the parameter of adsorption isotherm for carbon steel in 1M H_2SO_4 solution in different concentrations of inhibitor (Ib) at (308-338) K

T/K	$(1/T)*10^{-3}$ (K^{-1})	C/M	θ	C/θ	K_{ads} (M^{-1})	r^2
308	3.2	1.5×10^{-4}	0.8936	0.00017	100000	0.9999
		3.5×10^{-4}	0.9236	0.00038		
		4.6×10^{-4}	0.9280	0.00050		
318	3.1	1.5×10^{-4}	0.9398	0.00016	100000	1
		3.5×10^{-4}	0.9759	0.00036		
		4.6×10^{-4}	0.9759	0.00047		
328	3.0	1.5×10^{-4}	0.9541	0.00016	100000	1
		3.5×10^{-4}	0.9830	0.00036		
		4.6×10^{-4}	0.9831	0.00047		
338	2.9	1.5×10^{-4}	0.8563	0.00018	25000	0.9992
		3.5×10^{-4}	0.9851	0.00036		
		4.6×10^{-4}	0.9831	0.00047		

The high correlation facter (r^2) of the Langmuir adsorption isotherm may confirm the validity of this approach. The equilibrium constant (K_{ads}) for the adsorption–desorption process of tested inhibitor can be calculated from reciprocal of the intercept. The adsorptive equilibrium constant (K_{ads})values are listed in Table 7. Data in Table 7 also revealed that the adsorptive equilibrium constant (K_{ads}) slightly increase in the temperature rang 308–328 k.

(vi) Thermodynamic parameters of adsorption

The standard free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation [42]:

$$\Delta G_{ads} = -2.303RT\log(55.5K_{ads}) \qquad (8)$$

where R is the gas constant, T is the absolute temperature and the value 55.5 is the concentration of water in solution expressed in M, K_{ads} is the equilibrium constant of the inhibitor adsorption process .Values of ΔG_{ads} are listed in Table 8. The values of ΔG_{ads} negative sign are usually characteristic of a strong interaction and a high efficient adsorption. Generally, values of ΔG_{ads} around -20 kJ mol^{-1} or lower negative are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Whereas, the more negative values than -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [43]. Calculated ΔG_{ads} values indicate that the adsorption mechanism of the synthesized inhibitor on carbon steel in 1M H_2SO_4 solution is chemical adsorption.

From the plotting of log K_{ads} vs. 1/T, the heat of adsorption (ΔH_{ads}), which is obtained from the slope of the linear portion of the curve, is equal to $-\Delta H_{ads}$ / 2.303R. The value of ΔH_{ads} is equal to enthalpy of adsorption (ΔH_{ads}) with good approximation, because pressure is constant.The ΔH_{ads} value of the synthesized inhibitor is equal to 29.146 kJ mol^{-1}. The positive value of ΔH_{ads} indicates that the adsorption of investigated inhibitor on the carbon steel surface is endothermic. An endothermic adsorption process ($\Delta H_{ads} > 0$) is due to chemisorptions while an exothermic one ($\Delta H_{ads} < 0$) may be attributed to physisorption, chemisorption or a mixture of both [44]. In an exothermic process, physisorption can be distinguished from chemisorption by considering the absolute value of ΔH_{ads}. For physisorption,ΔH_{ads} is lower than 40 kJ.mol^{-1} while for chemisorption, ΔH_{ads} approaches 100 kJ.mol^{-1} [45].

Entropy of inhibitor adsorption (ΔS_{ads}) is calculated using the following equation [46]:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (9)$$

Values of ΔS_{ads} are listed in table (8). It is observed that, ΔS_{ads} values in the presence of the inhibitor are positive sign, which mean that, an increase of disorder is due to the adsorption of only one inhibitor molecule by desorption of more water molecules [47].

Table 8- The thermodynamic parameters of adsorption of the synthesized inhibitor (Ib) at different concentrations for carbon steel in 1M H_2SO_4 solution.

T/K	ΔG_{ads} KJ.mol^{-1}	ΔH_{ads} KJ.mol^{-1}	ΔS_{ads} J.mol^{-1}.k^{-1}
308	-39.77	34.46	241.00
318	-41.06		237.48
328	-42.36		234.20
338	-39.75		219.55

(vii)Effect of temperature

To investigate the mechanism of inhibition and to determine the activation energy of the corrosion process, polarization curves of carbon steel in 1 M H_2SO_4 were determined at various temperatures (308–338 K) in the absence and presence of concentration range of (1.5×10^{-4} – $4.6\times10^{-4)}$ M (Ib) inhibitor. Inspection of Table 9, reveals that the corrosion rate decreases and hence %IE increases as the temperature increases Figure 5. This indicates that the rising of temperature increases the inhibition process, and the highest inhibition efficiency is obtained with 3.5×10^{-4} M (Ib) at 338 K. in case of 1.5×10^{-4} M the inhibition efficiency decrease at 338 K because domination of desorption process more than adsorption.

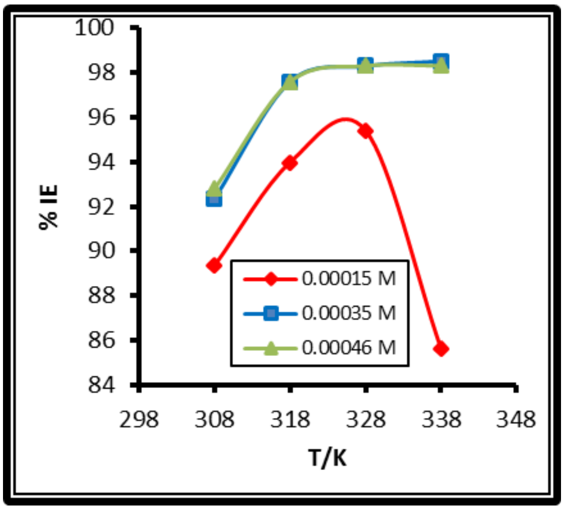


Figure 5- Relationship between inhibition efficiencies and different temperature(308-338) K for carbon steel in 1M H_2SO_4 for inhibitor(Ib)

Table 9- The effect of temperature on the corrosion parameters of carbon steel in 1 M H_2SO_4 containing different concentrations of inhibitor(Ib)

Conc. (M)	**Temp . K**	**E_{corr} Mv (SCE)**	**I_{corr} µA/cm^2**	**βc mV/dec**	**βa mV/dec**	**W.L g/m^2.d**	**Penetration loss mm/a**	**θ**	**% IE**
0	308	-411.8	1450	-109.2	70.5	363	16.9	--	--
	318	-394.7	6150	-134.4	102.6	1540	71.4		
	328	-381.2	13390	-153.6	128.8	3350	155		
	338	-372.3	21510	-243.2	137.4	5380	250		
1.5×10^{-4}	308	-442.7	154.26	-65.6	52.5	38.6	1.79	0.89	89.36
	318	-446.8	369.88	-77.7	73.5	92.511	4.29	0.93	93.98
	328	-455.0	613.41	-42.3	45.5	53	7.12	0.95	95.41
	338	-457.9	3090	-79.8	78.5	773	35.9	0.85	85.63
3.5×10^{-4}	308	-452.2	110.78	-75.5	80.2	27.7	1.29	0.92	92.36
	318	-432.5	148.18	-81.6	73.3	37.0	1.72	0.97	97.59
	328	-436.3	226.56	-62.1	65.7	56.6	2.63	0.98	98.30
	338	-430.2	320.39	-46.0	47.5	80.1	3.72	0.98	98.51
4.6×10^{-4}	308	-435.6	104.31	-66.8	53.6	26.1	1.21	0.92	92.80
	318	-434.6	147.62	-72.9	67.5	36.9	1.71	0.97	97.59
	328	-432.9	225.30	-60.7	59.0	56.3	2.62	0.98	98.31
	338	-425.5	363.35	-72.8	55.6	90.8	4.22	0.98	98.31

(viii) Activation parameters

The values of activation energy (Ea) were calculated from modified Arrhenius equation [39]:

$$\log i_{corr} = \log A - \frac{E_a^*}{2.303RT} \qquad (10)$$

Where i_{corr} is the corrosion current density, E_a^* is the apparent activation energy of the corrosion reaction, R is the gas constant, T is the absolute temperature and A is the Arrhenius pre-exponential factor. Figure 6 presents the Arrhenius plots of the natural logarithm of the current density *vs* 1/T, for 1M solution of H_2SO_4, in presence and absence of different concentrations of compound (Ib). Values of E_a^* and A for the corrosion reaction in the absence and presence of different concentrations of the (Ib) inhibitor are calculated by a linear regression method and given in Table 10. It is found that the activation energy is lower in the presence of inhibitor than in its absence.

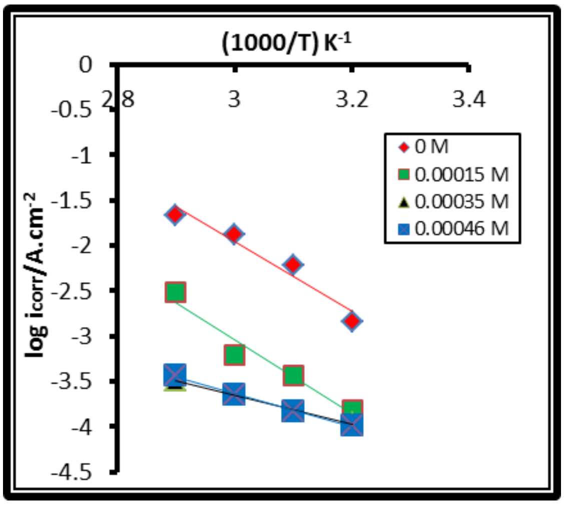


Figure 6- Arrhenius plots of log i_{corr} versus 1/T in presence and absence of different concentrations of compound (Ib)

E_a^* decreases with increasing the synthesized inhibitor (Ib) concentration. It is obvious that concentration of the synthesized inhibitor is playing a role in decreasing the activation energy value, thereby indicating a more efficient inhibiting effect. The decrease in E_a^* with the synthesized inhibitor concentration is typical of chemisorption process [48].This was attributed by Hoar and Holliday [49] to a slow rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at the higher temperature. But, Riggs and Hurd

[50] explained that the decrease in activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from that on the uncovered part on the metal surface to the covered one. Schmid and Huang [51] found that organic molecules inhibit both the anodic and cathodic partial reactions on the electrode surface and a parallel reaction takes place on the covered area, but that the reaction rate on the covered area is substantially less than on the uncovered area like that in this work Table 10. According to Eq. (10) low values of A and high values of E_a^* lead to lower corrosion rates. For the present study, E_a^* is lower in the presence of (Ib). Therefore, the decrease in the steel corrosion rate is decided by the pre-exponential factor A.

Table 10- The thermodynamic parameters of activation of the synthesized inhibitor (Ib) at different concentrations for carbon steel in 1M H_2SO_4

Conc. (M)	**A ($A.cm^{-2}$)**	**E_a^* ($KJ.mol^{-1}$)**
0	3.96×10^{9}	73.74
1.5×10^{-4}	2.14×10^{9}	78.92
3.5×10^{-4}	1126×10^{-2}	30.02
4.6×10^{-4}	6211×10^{-2}	34.64

4. Conclusion

The inhibiting effect of sulphanyl benzimidazole derivatives (Ia-c) in 1 M H_2SO_4 on carbon steel was studied by various methods. The results are good and the main conclusions are as follows:

1) The chemical structure of the synthesized inhibitors are confirmed by FTIR,^{1}H- NMR and ^{13}C-NMR.
2) The corrosion inhibition efficiency (**%** IE) of sulphanyl benzimidazole derivatives follows the sequence: Ib > Ic > Ia The inhibition efficiency of these compounds increased by increasing the electron donor characteristic of the substituted groups.
3) Ib was found to be the best inhibitor for carbon steel in 1M H_2SO_4.
4) The inhibition efficiency of Ib increases with increase of inhibitor concentration. Its presence in the solution decreases the value of the apparent activation corrosion energy.
5) The adsorption of Ib on the steel surface in sulphuric acid obeys the Langmuir adsorption isotherm model and leads to the formation of a protective film.
6) The analysis of the experimental data leads to the suggestion of chemisorption of the inhibitor on the metal surface. In fact, the apparent activation energy of the corrosion that is lower in presence of Ib than in its absence and the higher values of the free energy of adsorption verify the chemisorptive character of the adsorption.
7) The substance is adsorbed with the heteroatoms forming donor–acceptor bonds between unpaired electrons of the heteroatoms and the active centres of the metal surface.

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