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Substitution Effect of two Oxygen Atoms by Sulphur Atoms in New Synthesized Benzodiazepine Molecules towards Mild Steel Corrosion Inhibition in Hydrochloric Acid

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The corrosion inhibition of mild steel in molar HCl by two newly synthesized benzodiazepine derivatives, namely: 10-benzyl-pyrrolo[2,1-*c*][1,4]benzodiazepine-5,11-dione (BZD=2O), and 10-benzyl-pyrrolo[2,1*c*][1,4]benzodiazepine-5,11-dithione (BZD=2S); has been investigated at 308 K using electrochemical and weight loss measurements. The results showed that these compounds were good inhibitors and the inhibiting efficiency increased with rise concentration of the studied inhibitors. Compound BZD=2S showed better protection properties even at higher temperatures. BZD=2S was adsorbed on the mild steel surface according to a Langmuir isotherm adsorption model. The associated kinetic and thermodynamic parameters for both metal dissolution and inhibition processes have been determined and discussed.

Keywords: Benzodiazepine; Corrosion inhibition; Mild steel; Hydrochloric acid; Adsorption

1. INTRODUCTION

A benzodiazepine (sometimes colloquially "benzo"; often abbreviated "BZD") is a

psychoactive drug whose core chemical structure is the fusion of a benzene ring and a diazepine ring. The first benzodiazepine, chlordiazepoxide (Librium), was discovered accidentally by Leo Sternbach in 1955, and made available in 1960 by Hoffmann–La Roche, which has also marketed diazepam (Valium) since 1963 [1]. The benzodiazepine compounds seem to present also the most properties to act as corrosion inhibitors. Indeed, efficient inhibitors are organic compounds having π and/or n bonds in their structures. The inhibiting effect of an organic molecule, as a successful inhibitor, is mainly dependent on its ability to get on the metal surface which consists of the replacement of water molecules at the corroding interface.

These hetero-atoms, such as sulphur, phosphorus, nitrogen, and oxygen, together with heterocyclic or conjugated aromatic, play significantly in inhibition process [2-6]. Furthermore, the most synthesised compounds are the nitrogen-heterocyclic compounds which are known to be excellent complex or chelate forming substances with metals of transition series. Their adsorption is generally explained by the formation of an adherent film on the metal surface [7–11].

The introduction of sulphur atom in heterocyclic compounds containing nitrogen has proved very good corrosion inhibition of metals in acidic solutions [12–14]. Their inhibitive power is related to the various active adsorption centres as cyclic rings or hetero-atoms. The higher inhibition efficiency of hetero-atoms as oxygen, nitrogen, phosphorus and sulphur should follow the sequence O<N<S<P [14].

Although the most effective organic inhibitors, the biological toxicity of these products is documented especially about their environmental harmful characteristics [15,16]. From the standpoint of safety, the development of non-toxic and effective inhibitors is of considerable interest. Nowadays, researches seem to retain many attempts and are focused on the use of two Benzodiazepine compounds.

The aim of the present study was to evaluate the corrosion inhibition efficiency and analyse the inhibitive mechanism of mild steel corrosion in hydrochloric acid by two newly synthesized benzodiazepine compounds; namely, 10-benzyl-pyrrolo[2,1-*c*][1,4]benzodiazepine-5,11-dione and 10-benzyl-pyrrolo[2,1*c*][1,4]benzodiazepine-5,11-dithione and denoted hereafter BZD=2O and BZD=2S, respectively. The study was done using several weightless and electrochemical techniques such as ac impedance measurements and polarisation curves. The effect of temperature on the corrosion behaviour was also studied in the range from 313 K to 353 K. The thermodynamic parameters such as adsorption heat $\Delta_{ads}H°$, entropy of adsorption $\Delta_{ads}S°$ and adsorption free energy $\Delta_{ads}G°$ were calculated and discussed.

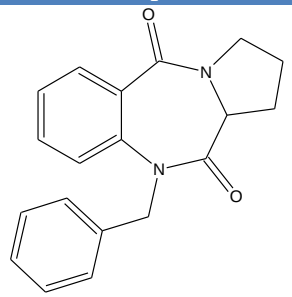
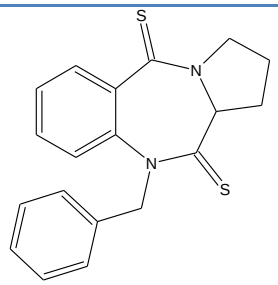
2. EXPERIMENTAL PROCEDURE

2.1. Material preparation

Mild steel strips containing 0.09 wt.% P, 0.38 wt.% Si, 0.01 wt.% Al, 0.05 wt.% Mn, 0.21 wt.% C, 0.05 wt.% S and balance iron were used for electrochemical and gravimetric studies. Mild steel specimens were mechanically polished on wet SiC paper (400, 600, 1000 and 1200), washed with

double-distilled water, degreased ultrasonically in ethanol, and finally dried at room temperature before being immersed in the acid solution. The temperature was controlled at 308 K. The acid solutions used were made from Riedel-de Haën. Appropriate concentrations of inhibitors were prepared with double-distilled water addition. The concentration range of inhibitors employed was 10^{-6} – 10^{-3} M in 1 M HCl. Table. 1 shows the molecular structures of the investigated organic compounds BZD=2O and BZD=2S, which were prepared according to the literature procedure [17-18].

Table 1. Molecular structures, names and abbreviations of the studied benzodiazepine compounds.

Benzodiazepine Formula	Name	Abbreviation
	10-benzyl-pyrrolo[2,1-*c*][1,4]benzodiazepine-5,11-dione	BZD=2O
	10-benzyl-pyrrolo[2,1-*c*][1,4]benzodiazepine-5,11-dithione	BZD=2S

2.2. Electrochemical measurements

Potentiodynamic polarization curves measurements were carried out by a Potentiostat Radiometer-analytical PGZ 100 and controlled with analysis software (Voltamaster 4). The experiments were carried out in a conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. The mild steel electrode, kept at its open circuit value, was polarized at -800 mV for 10 min. The potential of the electrode was then swept to more anodic potentials.

Inhibition efficiencies were calculated from corrosion currents densities determined from Tafel extrapolation method. The inhibiting efficiency was derived from the equation (1):

$$E_I\,\% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (1)$$

Where I_{corr} and I'_{corr} are the corrosion current densities values without and with inhibitors, respectively and determined by extrapolation of cathodic Tafel lines to the corrosion potential, E_{corr}.

Electrochemical impedance spectroscopy (EIS) was performed using a transfer function analyser (Voltalab PGZ 100), with a small amplitude a.c. signal (10 mV rms) over a frequency domain from 100 kHz to 10 mHz at 308 K with five points per decade. Computer programmed automatically and controlled the measurements performed at rest potentials after half an hour of immersion at E_{corr}. The impedance diagrams were given in the Nyquist representation.

2.3. Weight loss measurements

Gravimetric experiments were carried out in a double-walled glass cell. The solution volume was 100 cm^3 and the temperature of 308 K was controlled thermostatically. The weight loss of mild steel in 1 M HCl with and without addition of BZD=2O and BZD=2S inhibitors was determined after an immersion period in acid for 6 h. The mild steel specimens were in square form (2cm×2cm×0.05cm). Corrosion efficiencies (E_w%) were calculated according to the equation (2):

$$E_W\,\% = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \times 100 \qquad (2)$$

W_{corr} and $W_{corr/inh}$ are the corrosion rate of mild steel without and with BZD=2O and BZD=2S inhibitors, respectively.

3. RESULTS AND DISCUSSION

3.1. Polarization curves

Curves, obtained in the presence and absence of BZD=2O and BZD=2S, after pre-polarizing the electrode at its E_{corr} for 30min, are shown in Figure 1.

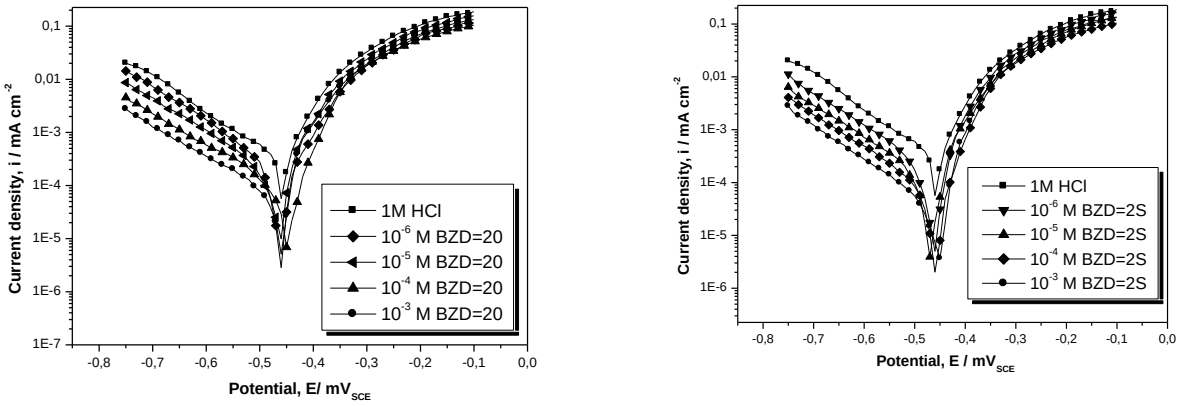


Figure 1. Polarization curves for mild steel in 1 M HCl at different concentrations of the studied molecules BZD=2O and BZD=2S.

The potential was swept stepwise from the most cathodic potential to the anodic direction; this avoided electrolyte pollution by dissolved iron. Table 2 exemplifies the values of the associated electrochemical parameters (corrosion potentials (E_{corr}), cathodic Tafel slopes (β_c), corrosion current densities (I_{corr}) and inhibiting efficiencies (E_I%).

The examination, of Fig. 1 and results reported in Table 2, shows that the addition of BZD=2O and BZD=2S compounds decreases markedly current density on the cathodic branch whereas little decrease is registered in the anodic branch and the decrease is more pronounced with the increase of the inhibitor concentrations. The corrosion potential seems to be unchanged despite addition of BZD=2O and BZD=2S inhibitors. These results suggest that BZD=2O and BZD=2S mainly act as mixed-type inhibitors with marked cathodic behaviour. Moreover, it appears that the cathodic current-potential curves give rise to parallel Tafel lines, indicating that the hydrogen evolution reaction is under activation control. Cathodic Tafel slopes β_c were approximately constant, meaning that the inhibiting actions of BZD=2O and BZD=2S molecules occurred by simple blocking of the available surface area; i.e., the inhibitors decrease the surface area for hydrogen evolution without affecting the reaction mechanism [19].

Table 2. Polarization parameters and corresponding inhibition efficiencies for the corrosion of the mild steel in 1 M HCl without and with addition of various concentrations of benzodiazepine compounds BZD=2O and BZD=2S.

Inhibitor	Concentration mol L^{-1}	E_{corr} mV_{sce}	$\lvert\beta_c\rvert$ mV dec^{-1}	I_{corr} µA cm^{-2}	E_I %
Blank	00	-460	160	350	-
BZD=2O	1 x 10^{-6}	-460	155	220	37.1
	1 x 10^{-5}	-460	160	147	58.0
	1 x 10^{-4}	-450	176	92	73.7
	1 x 10^{-3}	-460	176	54	84.6
BZD=2S	1 x 10^{-6}	-460	160	192	45.1
	1 x 10^{-5}	-470	163	125	64.3
	1 x 10^{-4}	-460	160	70	80.0
	1 x 10^{-3}	-450	156	30	91.4

From Table 2, it can be concluded that the inhibition efficiency E_I% increases with inhibitors concentration, reaching the values of 84.6 % and 91.4 % at 10^{-3} mol L^{-1} of BZD=2O and BZD=2S, respectively. The increase in inhibition efficiency observed at higher inhibitors concentration indicates that more inhibitor molecules are adsorbed (see the sections below) on the metal surface thus providing wider surface coverage then these compounds are acting as adsorption inhibitors [20].

3.2. EIS measurements

A better understanding of the mechanism taking place at the electrode surface is attained through EIS measurements. The EIS impedance is performed under potentiostatic conditions at E_{corr} and 308 K in the uninhibited and inhibited acidic solution containing various concentrations of

BZD=2O and BZD=2S. Before each measurement, the electrode is left at the open circuit conditions during 30 min. The electrode system does not evolve significantly during the impedance measurements. The impedance diagrams obtained are characterized by one capacitive loop (Figure 2).

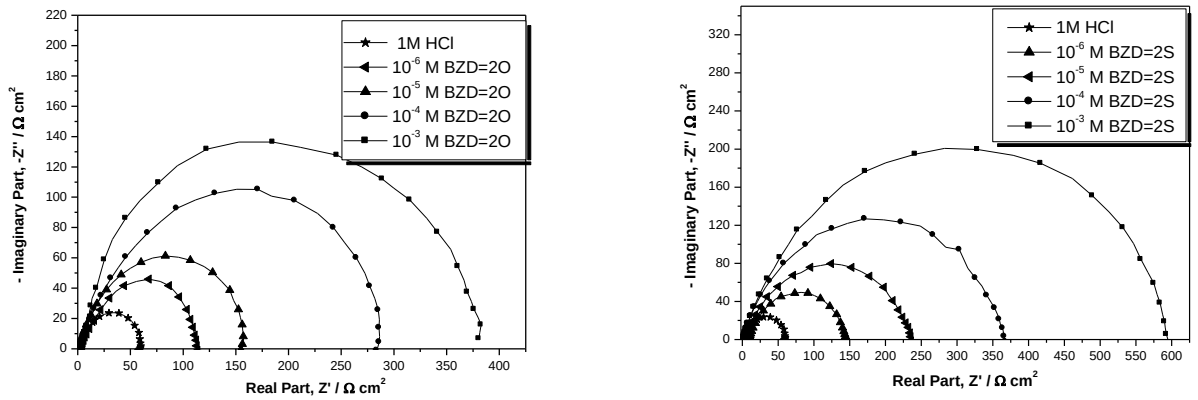


Figure 2. Nyquist diagrams for mild steel in 1M HCl without and with different concentrations of the undertaken inhibitors BZD=2O and BZD=2S.

It is clear from these spectra that the impedance response of mild steel in the absence of inhibitors has significantly changed after the addition of BZD=2O and BZD=2S in the corrosive medium. Indeed, the impedance of inhibited electrode increases with increasing inhibitors concentration and consequently the inhibition efficiency increases as it is explained hereafter.

A depressed semicircle, as often obtained in acidic media [21,22] can be seen. The difference from theoretical results is generally attributed to Cole-Cole [23] and/or Cole-Davidson [24] representations inherent to frequency dispersion. This phenomenon is generally attributed to different physical processes such as the non homogeneity of the electrode surface or its roughness during the corrosion process [25,26], adsorption of inhibitors [27], and formation of porous layers [28,29]. The existence of single semicircle relates the presence of single charge-transfer process, which is unaffected by the presence of BZD=2O and BZD=2S. According to a classical method, the EIS spectra of Figure 2 will be interpreted in terms of parallel R_t-C_d circuit; i.e., one time constant τ_t.

Table 3 summarizes the impedance parameters at different concentrations of BZD=2O and BZD=2S in 1 M HCl, respectively and the values of the inhibition efficiency $E_R\%$. The charge transfer resistance (R_t) values are calculated from the difference in impedance at low and high frequencies while the double layer capacitance (C_d) was obtained at the frequency f_{max} on the apex of the imaginary component of the impedance $(-Z''_{\max})$ by equation (3):

$$f(-Z''_{\max}) = \frac{1}{2\pi\tau_t}, \ \ where\ \tau_t = R_t C_d \qquad (3)$$

$E_R\%$ got from the charge transfer resistance is calculated by equation 4:

$$E_R\ \% = \frac{R_{t/inh} - R_t}{R_{t/inh}} \times 100 \quad (4)$$

Where R_t and $R_{t/inh}$ are the charge-transfer resistance values without and with BZD=2O and BZD=2S inhibitors, respectively.

Table 3. Impedance parameters of mild steel in 1M HCl containing different concentrations of the studied benzodiazepine compounds.

Inhibitor	Concentration mol L^{-1}	R_{ct} Ω cm^2	f_{max} Hz	C_{dl} μF cm^{-2}	E_R %
Blank	00	60	20	133	–
BZD=2O	1 x 10^{-6}	115	15.82	88	47.8
	1 x 10^{-5}	155	12.5	82	61.3
	1 x 10^{-4}	280	7.93	71	78.6
	1 x 10^{-3}	380	7.93	52	84.2
BZD=2S	1 x 10^{-6}	145	15.82	69	58.6
	1 x 10^{-5}	240	12.5	53	75.0
	1 x 10^{-4}	370	10	43	83.8
	1 x 10^{-3}	600	7.93	33	90.0

From the impedance parameters, one can conclude that the value of R_t increases with concentration increase of BZD=2O and BZD=2S and this indicates an increase in the corrosion inhibition efficiency. This indicates that the charge-transfer process mainly control the corrosion of mild steel. The values of double layer capacitance are brought down to the maximum extend in the presence of BZD=2O and BZD=2S and the decrease of C_d follows the order similar to that obtained for I_{corr} obtained from *I-E* characteristics. If one assumes that the double layer between the charged surface and the electrolyte is considered as an electrical capacitor, the adsorption of benzodiazepine on the electrode may decrease the electrical capacity because the inhibitor displaces the water molecules or even others ions originally adsorbed on the electrode. Thus the decrease of C_d with rise in concentration of BZD=2O and BZD=2S is in favour of selectively adsorption of BZD=2O and BZD=2S in specific places and/or formation of complex onto the metal surface. According to this inhibition mechanism, BZD=2O and BZD=2S can be adsorbed at active points causing the corrosion rate to drop.

The values of inhibition efficiencies obtained from EIS measurements for the tested inhibitors follow the order BZD=2S > BZD=2O. The EIS results correspond to those obtained from polarization tests.

3.3. Weight loss measurements

The values of inhibition efficiencies and corrosion rates obtained from weight loss method in the absence and presence of various concentrations of BZD=2O and BZD=2S are given in Table 4. From these data, it is evident that for the studied inhibitors, the corrosion rate W_{corr} of mild steel decreases

with increase of concentration. Moreover, the protection efficiency increases with increasing the concentration of both benzodiazepine derivatives. The corrosion inhibition can be attributed to the adsorption of the studied inhibitors at the mild steel/acid solution interface. Maximum of $E_R\%$ for each compound is achieved at 10^{-3} M and any further increase in concentration do not cause appreciable change in the performance of inhibitors.

Table 4. Corrosion rate of steel and inhibition efficiency at different concentrations of benzodiazepine derivatives for the corrosion of steel in 1 M HCl obtained from weight loss measurements at 308 K after 6 h of immersion.

Inhibitor	Concentration C / mol L^{-1}	Corrosion weight loss W_{corr} / mg cm^{-2} h^{-1}	E_W %	Surface Coverage θ
Blank	00	1.15	–	
BZD=2O	1 x 10^{-6}	0.74	35.7	0.357
	1 x 10^{-5}	0.61	47.0	0.470
	5 × 10^{-5}	0.42	63.5	0.635
	1 x 10^{-4}	0.32	72.2	0.722
	5 × 10^{-4}	0.19	83.5	0.835
	1 x 10^{-3}	0.12	89.6	0.896
BZD=2S	1 x 10^{-6}	0.70	39.1	0.391
	1 x 10^{-5}	0.56	51.3	0.513
	5 × 10^{-5}	0. 26	77.4	0.774
	1 x 10^{-4}	0.19	83.5	0.835
	5 × 10^{-4}	0.09	92.2	0.922
	1 x 10^{-3}	0.05	95.6	0.956

The variation in inhibiting efficiency mainly depends on the type and the nature of the substitution in the inhibitor molecule. The ability of the molecule to adsorb on the mild steel surface is dependent on the presence of sulphur atom (S) on BZD=2S which arise an enhancement in the inhibiting efficiency. It is apparent that the adsorption of these compounds on the metal surface can occur directly on the basis of donor acceptor interaction between the lone pairs of the heteroatom and extensively delocalised π-electrons of the benzodiazepine derivatives and the vacant d-orbital of iron surface atoms [30,31]. The same effect has been observed by Zerga et al. for the study of four organic compounds of pyridazine type [32].

The results obtained from the weight loss measurements are in agreement with those obtained from linear polarization method and EIS measurements.

3.4. Effect of temperature

The temperature can modify the interaction between the mild steel electrode and the acidic medium in the absence and in the presence of inhibitors. Weight loss measurements for mild steel in 1 M HCl at different concentrations of the best inhibitor BZD=2S, in the temperature range 313–353 K, are shown in Table 5.

The corrosion rates increase with rise of temperature both in uninhibited and inhibited solutions. Moreover, the mild steel corrosion increased more rapidly with temperature in the absence

of BZD=2S. Therefore, the values of inhibition efficiencies of BZD=2S remains constant with temperature increase; the protective properties are very good even at 353 K (90.9%). These results confirm that BZD=2S acts as the better inhibitor in the studied range temperature. The BZD=2S inhibitor efficiency is then nearly temperature–independent.

The corrosion reaction can be regarded as an Arrhenius-type process, eq. (5) [33]:

$$W_{corr} = Ae^{-\frac{E_a}{RT}} \quad (5)$$

W_{corr} is the corrosion rate, A is the Arrhenius pre-exponential constant and E_a is the activation corrosion energy for the corrosion process:

Table 5. Effect of temperature on the corrosion rate of mild steel in 1 M HCl without and with BZD=2S at different concentrations and the corresponding corrosion inhibition efficiencies.

Temperature T / K	Concentration C / mol L^{-1}	Corrosion weight loss W_{corr} / mg cm^{-2} h^{-1}	E_W %
313	00	1.3	–
	5×10^{-5}	0.29	77.7
	1×10^{-4}	0.22	83.1
	5×10^{-4}	0.13	89.2
	1×10^{-3}	0.098	92.5
323	00	3.47	–
	5×10^{-5}	0.79	77.2
	1×10^{-4}	0.60	82.7
	5×10^{-4}	0.35	89.9
	1×10^{-3}	0.26	92.5
333	00	6.72	–
	5×10^{-5}	1.53	77.2
	1×10^{-4}	1.25	81.4
	5×10^{-4}	0.68	89.8
	1×10^{-3}	0.56	91.6
343	00	10.8	–
	5×10^{-5}	2.48	77.0
	1×10^{-4}	2.05	81.0
	5×10^{-4}	1.13	89.5
	1×10^{-3}	0.94	91.3
353	00	19.2	–
	5×10^{-5}	4.45	76.8
	1×10^{-4}	3.61	81.2
	5×10^{-4}	2.07	89.2
	1×10^{-3}	1.75	90.9

Activation parameters for the corrosion process are calculated using the alternative formulation of Arrhenius equation called transition state, eq. (6) [34]:

$$W_{corr} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (6)$$

Where k_B is the Boltzmann's constant (k_B = 1.38066 10^{-23} J K^{-1}), h is the Planck's constant (h = 6.6252 10^{-34} J s) and ΔH^* and ΔS^* are the enthalpy and the entropy of corrosion process activation, respectively.

The apparent activation energies E_a at different concentrations of benzodiazepine derivative are calculated by linear regression between lnW_{corr} vs. $1/T$ (Fig. 3) and the results are shown in Table 6. The values of E_a, determined in the presence of BZD=2S, are higher than in free solution (blank). The E_a value corresponds to that of hydrogen ions activation and in fact can be considered as a verification of the corrosion process [35].

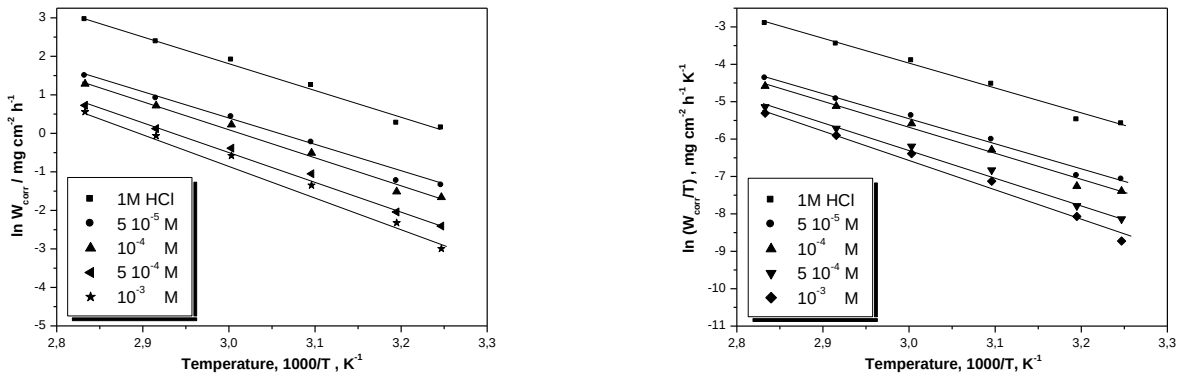


Figure 3. Verification of the Arrhenius equation (left plot) and the alternative formula of Arrhenius equation (right plot) at different concentrations of BZD=2S inhibitor in 1 M HCl.

The temperature dependence of the inhibiting effect and the comparison of the values of the apparent activation energy of the corrosion process in absence and presence of BZD=2S can provide further evidence [36] concerning the mechanism of the inhibiting action. The lower value of E_a in an inhibited solution when compared to that for uninhibited shows that strong chemisorption bond between the inhibitor and the metal is highly probable.

Table 6. Activation parameters E_a, ΔH^* and ΔS^* of mild steel dissolution process in 1 M HCl in the absence and the presence of BZD=2S at different concentrations.

Inhibitor	Concentration C / mol L^{-1}	E_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* J K^{-1} mol^{-1}
Blank	00	58.71	55.97	-62.94
BZD=2S	5×10^{-5}	59.32	56.58	-73.41
	1×10^{-4}	61.65	58.93	-68.28
	5×10^{-4}	63.29	60.54	-68.31
	1×10^{-3}	69.89	67.18	-50.50

Hence it can be suggested that BZD=2S adsorb on the metal surface forming strong chemisorption bonds. This is in fact possible in view of the presence of unshared electron pairs in the

organic compounds molecules and taking into consideration the behaviour of iron as electrons acceptor as its d-submonolayer is incomplete.

Figure 3 shows the plot of $ln(W_{corr}/T)$ against $1/T$. Straight lines are obtained with a slope of $(-\Delta H^*/R)$ and an intercept of ($ln\ k_B/h + \Delta S^*/$R), which give the values of ΔH^* and ΔS^*. Inspection, of the values of ΔS^* and ΔH^* in Table 6, reveals that the thermodynamic parameters ΔH^* of the dissolution reaction of steel in 1 M HCl in the presence of BZD=2S are higher than that of in the absence of BZD=2S. The positive sign of the enthalpies ΔH^* reflects the endothermic nature of the mild steel dissolution process and mean that the dissolution of steel is difficult [37]. Also, the entropy ΔS^* takes negative values in the presence of the BZD=2S and increases with concentration rise of BZD=2S.

3.5. Adsorption isotherm

Important information about the interaction between the inhibitor and mild steel surface can be provided by the adsorption isotherm. From the above results, it can be concluded that the surface coverage θ assumed to $E_W\%/100$ increases with the inhibitor concentration; this maybe imputed to more adsorption of inhibitor molecules onto the steel surface. As it is known, the adsorption of inhibitor is always a displacement reaction involving removal of absorbed water molecules from the metal surface [38], eq. (7):

$$Org\ (sol) + nH_2O\ (ads) = Org\ (ads) + nH_2O\ (sol) \quad (7)$$

Where Org (sol) and Org (ads) are the organic molecules in the aqueous solution and adsorbed on the steel surface, respectively. H_2O (ads) is the water molecule on the steel surface and n reflects the size ratio representing the number of water molecules replaced by one unit of organic inhibitor.

Now, assuming that the adsorption of benzodiazepine belonged to the monolayer adsorption, then the Langmuir adsorption isotherm is applied to investigate the mechanism by the equation (8) [39]:

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \text{ with } \Delta_{ads}G^\circ = -RT\ln 55.55K_{ads} \quad (8)$$

Where K_{ads} is the adsorption coefficient and $\Delta_{ads}G^\circ$ is the standard free energy of adsorption value of BZD=2S at different temperatures.

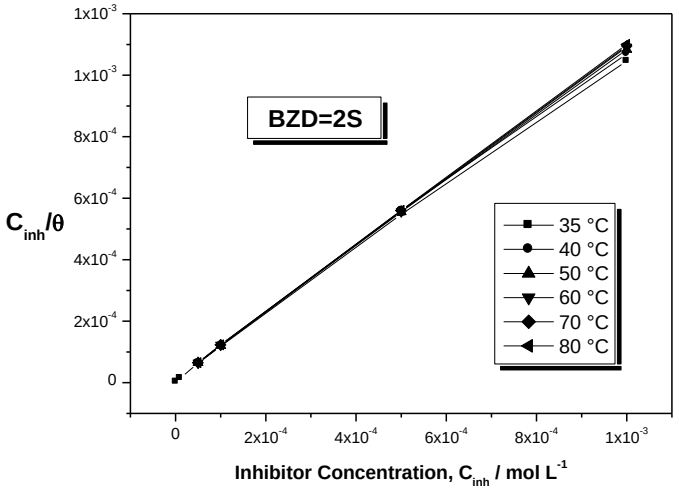


Figure 4. Langmuir isotherm adsorption model on the steel surface of BZD=2S in 1 M HCl.

The plots of Fig. 4 reflecting the evolution C_{inh}/θ versus C_{inh} are with slope around unity which suggests that BZD=2S adsorbs on the metal surface obeying to the Langmuir's adsorption isotherm. Resulted in terms of $\Delta_{ads}G°$ equal to -39.46 kJ mol^{-1} at 313 K and -44.77 kJ mol^{-1} at 353 K (Table 7) in the range of studied temperatures. The low and negative value of $\Delta_{ads}G°$ indicates the spontaneous adsorption of BDZ=2S on the mild steel surface. This kind of isotherm, generally regarded to indicate chemisorption [40], involves the assumption of no interaction between the adsorbed species on the electrode surface [41].

Table 7. Thermodynamic parameters for the adsorption of BZD=2S in 1 M HCl on mild steel at different temperatures.

Temperature T/ K	Adsorption constante K_{ads}	$\Delta_{ads}G°$ kJ mol^{-1}	$\Delta_{ads}H°$ kJ mol^{-1}	$\Delta_{ads}S°$ J K^{-1} mol^{-1}
313	68823	-39.46	-0.55	124.8
323	71700	-40.83		
333	72158	-42.16		
343	72495	-43.40		
353	75260	-44.77		

Considering the values of enthalpy and entropy of the inhibition process have no distinct changes in the studied temperature range, the thermodynamic parameters $\Delta_{ads}H°$ and $\Delta_{ads}S°$ for the adsorption of BZD=2S onto the mild steel can be calculated from the integrated version of the Vant'Hoff isobar equation (9) expressed by [42]:

$$\ln K_{ads} = -\frac{\Delta_{ads}H°}{RT} + cons\tan te \qquad (9)$$

The plot of *ln* K_{ads} vs. *1/T* gives straight lines with slope of $(-\Delta_{ads}H^{\circ}/R)$ and an intercept of $(\Delta_{ads}S^{\circ}/R - \ln 55.55)$ when considering a combination of equation 8 and the thermodynamic equation $\Delta_{ads}G^{\circ} = \Delta_{ads}H^{\circ} - T\,\Delta_{ads}S^{\circ}$ (Fig. 5).

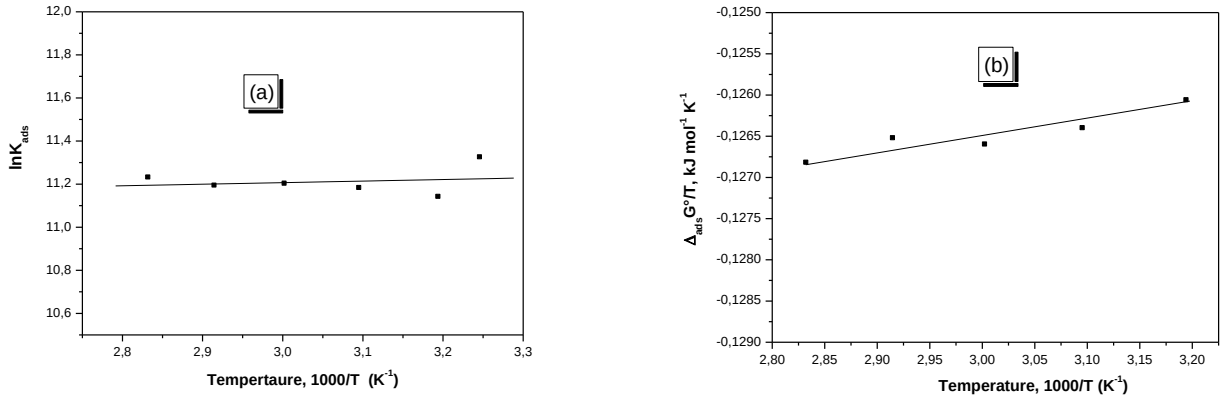


Figure 5. Vant'Hoff plot (a) and relationship between ΔG°_{ads}/T and 1/T (b) for the mild steel / BZD=2S system in 1 M HCl.

The negative sign of $\Delta_{ads}H^{\circ}$ indicates that the adsorption inhibitor molecules, is an exothermic process. $\Delta_{ads}S^{\circ}$ in presence of BZD=2S (Table 7) is large and positive meaning that an increase in disordering takes places in going from reactants to the metal-adsorbed species reaction complex [43]. It is to be noted that values of $\Delta_{ads}H^{\circ}$ and $\Delta_{ads}S^{\circ}$ derived from the plot of ΔG°_{ads}/T vs. 1/T are very comparable to those obtained from the plot *ln* K_{ads} vs. *1/T*.

4. CONCLUSIONS

The following main conclusions are drawn from the present study:

* The obtained results show the effectiveness of the investigated benzodiazepine compounds as good inhibitors for mild steel in 1 M HCl. The inhibition efficiency of the studied inhibitors increased with inhibitors concentration.

* The potentiodynamic measurements of BZD=2O and BZD=2S indicate that the studied inhibitors act as mixed-type inhibitors with marked cathodic behaviour retarding the cathodic process without changing the mechanism of hydrogen discharge.

* The electrochemical impedance study shows that the application of BZD=2O and BZD=2S inhibitors significantly increases the charge transfer values and decreases the double layer capacitance in 1 M HCl, suggesting that the corrosion inhibition takes place by adsorption.

* The inhibition performance of BZD=2S is found to be better than BZD=2O due to the presence of sulphur heteroatom.

* BZD=2S adsorbs on the metal surface obeying to the Langmuir's adsorption isotherm.

* The detailed study of BZD=2S shows that values of inhibition efficiencies remain constant with temperature increase. The apparent activation energy of corrosion process increases with rise of both temperature and concentration. The standard adsorption free energies are less negative than - 40 kJ mol^{-1}. These three results are in favour that the BDZ=2S is chemisorbed on mild steel surface.

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