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Electrochemical and Chemical Studies of some Benzodiazepine Molecules as Corrosion Inhibitors for Mild Steel in 1 M HCl

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The corrosion inhibition of mild steel in molar hydrochloric acid solution by : 2,3-dihydro-1H-pyrrolo[2,1c][1,4] benzodiazepine-5,11(10H,11aH)-dione (BZD1), 2,3-dihydro-1H-pyrrolo[2,1c][1,4] benzodiazepine-5,11(10H,11aH)-dithione (BZD2) and 3-phenyl-1,2,4-triazolo[3,4-c]pyrrolo[1,2a][1,4]benzodiazepine-9-thione (BZD3) has been investigated at 308 K using electrochemical and chemical methods. Current-voltage measurements showed that these compounds were good inhibitors without changing the mechanism of corrosion process. EIS measurements showed that the charge transfer resistance increases whereas the double layer capacitance decreases with the inhibitor concentration. The inhibiting efficiency increased with rise concentration of the studied inhibitors and was corroborated by the three undertaken techniques. BZD3 showed better protection properties even at relatively higher temperatures. The associated activation energy of corrosion process and standard free adsorption energies, for the best inhibitor BZD3, have been determined. BZD3 was adsorbed on the mild steel surface according to Langmuir isotherm adsorption model. Explanations by quantum chemical descriptors to be correlated with inhibition efficiency are under progress and should be published as soon as possible.

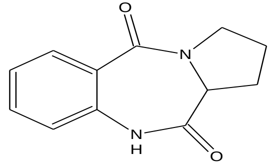
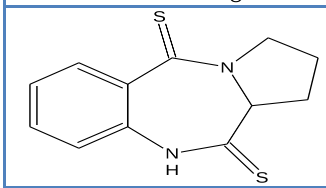
Keywords: Mild steel; Hydrochloric acid; Benzodiazepine; Corrosion inhibition; Adsorption

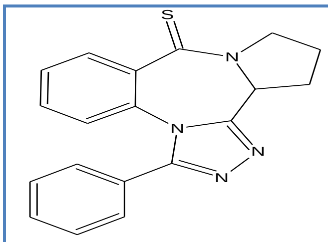
1. INTRODUCTION

The mild steel corrosion in acid media and especially in hydrochloric acid is often a very worrying problem for some industrial facilities. Indeed, several researchers devoted their attention to develop more effective and non-toxic inhibitors to reduce both acid attack and protection aspects [1-5]. The protective action of an inhibitor against metal dissolution is often associated with chemical and/or physical adsorption, involving a variation in the charge of adsorbed substances and a transfer of charge from one phase to the other. Special attention is paid to the electron density on the atom or on the group responsible of adsorption. The corrosion inhibition efficiency of organic compounds is generally connected to their adsorption properties. It has been observed that the adsorption mainly depends on the presence of π-electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the mild steel surface [6-9]. The benzodiazepine molecules seem to present the most properties to act as corrosion inhibitors. Indeed, 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 [10]. Moreover, data regarding the use of benzodiazepine derivatives are not so plentiful in acidic media [11].

The aim of the present study is to evaluate the corrosion inhibition efficiency and analyse the inhibitive mechanism of mild steel corrosion in 1 M HCl by: 2,3-dihydro-1H-pyrrolo[2,1c][1,4] benzodiazepine-5,11(10H,11aH)-dione, 2,3-dihydro-1H-pyrrolo[2,1c][1,4] benzodiazepine5,11 (10H,11aH)-dithione and 3-phenyl-1,2,4-triazolo[3,4-c]pyrrolo[1,2,a][1,4] benzodiazepine-9-thione, denoted hereafter BZD1, BZD2 and BZD3, respectively. Table 1 shows the molecular structures of the investigated organic compounds which were prepared according to the literature procedure [12,13]. The study is conducted using several weightless and electrochemical techniques such as ac electrochemical impedance and dc polarisation curves measurements. The effect of temperature on the corrosion behaviour, for the best inhibitor, is also studied in the range from 313 K to 353 K. The thermodynamic parameters, at standard state, such as adsorption heat $\Delta_{ads}H°$, adsorption entropy $\Delta_{ads}S°$ and adsorption free energy $\Delta_{ads}G°$ are calculated and discussed.

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

Benzodiazepine Formula	Name	Abbreviation
	2,3-dihydro-1H-pyrrolo[2,1c][1,4] benzodiazepine-5,11(10H,11aH)-dione	BZD1
	2,3-dihydro-1H-pyrrolo[2,1c][1,4] benzodiazepine-5,11(10H,11aH)-dithione	BZD2

	3-phenyl-1,2,4-triazolo[3,4c]pyrrolo[1,2a][1,4] benzodiazepine-9-thione	BZD3

2. EXPERIMENTAL PROCEDURE

2.1. Material preparation

Mild steel strips containing in wt. %: 0.09 P, 0.38 Si, 0.01 Al, 0.05 Mn, 0.21 C, 0.05 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.

2.2. Electrochemical measurements

Electrochemical measurements were done by (Radiometer-analytical PGZ 100) and controlled with analysis software (Voltamaster 4). Potentiodynamic polarization curves were carried out in a conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. All tests were performed in continuously stirred conditions on air at 308 K. The procedure adopted for the polarization measurements was the same as described elsewhere [14]. The cathodic branch was always determined first; the open circuit potential was then re-established and the anodic branch determined. The anodic and cathodic polarization curves were recorded by a constant sweep rate of 1 mV s^{-1}. Inhibition efficiencies were determined from corrosion currents densities and calculated from Tafel extrapolation method. The inhibiting efficiency was derived from 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 inhibitor, respectively and determined by extrapolation of cathodic Tafel lines to the corrosion potential.

The impedance spectra were recorded at the open circuit potential (OCP) in the frequency range from 100 kHz to 10 mHz with 10 points per decade at alternating current amplitude of ± 10 mV ac voltage peak-to-peak. Nyquist diagrams were made from these experiments and were in the form of semicircle. The best one can be fitted through the data points in the Nyquist representation using a non-linear least square fit so as to give the intersections with the real-axis. The effectiveness of corrosion got from the charge transfer resistance was calculated by equation 2:

$$E_R\% = \frac{R_{t/inh} - R_t}{R_{t/inh}} \times 100 \qquad (2)$$

where R_t and $R_{t/inh}$ are the charge transfer resistance values without and with inhibitor, respectively.

2.3. Chemical 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 inhibitors was determined after an immersion period in acid during 6 h. The mild steel specimens were rectangular in the form (2cm×2cm×0.05cm). The inhibiting efficiencies (E_w%) were calculated according to the equation 3:

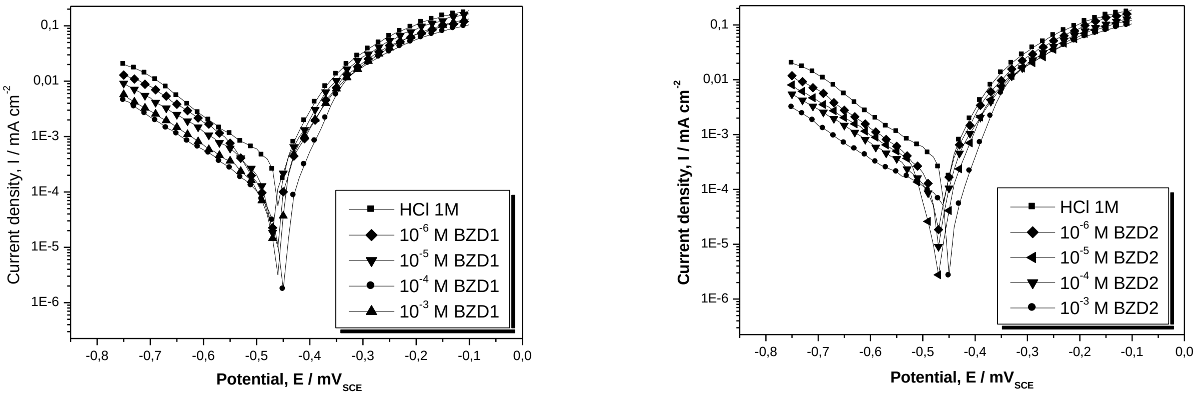
$$E_W\% = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \times 100 \qquad (3)$$

where W_{corr} and $W_{corr/inh}$ are the corrosion rate of mild steel without and with inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1. Polarization curves

Steady-state polarization curves, obtained in the presence and absence of BZD1, BZD2 and BZD3, after pre-polarizing the electrode at its E_{corr} for 1 h, are shown in Figure 1.



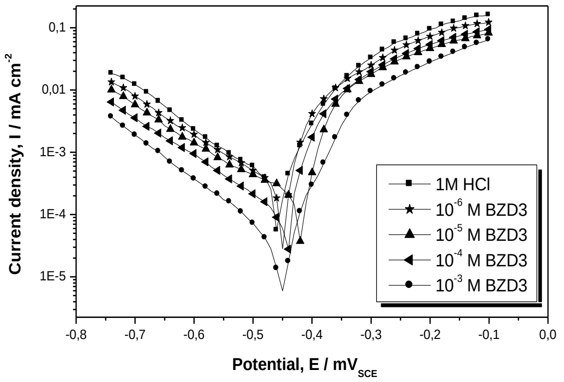


Figure 1. Polarization curves for mild steel in 1 M HCl at different concentrations of the studied molecules BZD1, BZD2 and BZD3.

Table 2. Polarization parameters and corresponding inhibition efficiency for the mild steel corrosion in 1 M HCl without and with addition of various concentrations of benzodiazepine molecules BZD1, BZD2 and BZD3.

Inhibitor	Concentration C / M	E_{corr} mV$_{sce}$	$\lvert\beta_c\rvert$ mV dec^{-1}	I_{corr} µA cm^{-2}	E_I %
Blank	00	-460	160	350	-
BZD1	1 x 10^{-6}	-460	159	278	20.6
	1 x 10^{-5}	-460	168	190	45.7
	1 x 10^{-4}	-460	165	107	69.4
	1 x 10^{-3}	-450	163	63	82.0
BZD2	1 x 10^{-6}	-470	150	200	42.8
	1 x 10^{-5}	-470	160	155	55.7
	1 x 10^{-4}	-470	162	100	71.4
	1 x 10^{-3}	-450	170	44	87.4
BZD3	1 x 10^{-6}	-450	166	238	32.0
	1 x 10^{-5}	-420	170	127	63.8
	1 x 10^{-4}	-440	165	62	82.3
	1 x 10^{-3}	-450	152	31	91.1

The potential is swept stepwise from the most cathodic potential to the anodic direction; this avoided electrolyte pollution by dissolved iron. From these results, it appears that the increase in inhibitor concentrations has no definite trend in the shift of corrosion potential values and remains globally almost constant. As it can be seen, both cathodic and anodic reactions of mild steel electrode corrosion are inhibited with the increase of inhibitor concentrations in 1 M HCl. However, the anodic branch, in the presence of BZD3, seems to be noticeably affected when compared to BDZ1 and BDZ2. Thus BZD3 acts as mixed-type inhibitor whereas BDZ1 and BDZ2 operate predominately as cathodic inhibitors. Moreover, Figure 1 indicates that cathodic current-potential curves give rise to Tafel lines, indicating that the hydrogen evolution reaction is activation-controlled. The anodic branch indicates that the inhibition mode of BZD3 does not depend upon electrode potential. Similar behaviour was observed in our earlier results [15] and with other co-workers [16,17].

The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (βc) derived from polarization curves, and the corresponding inhibition efficiency $E_I\%$ values at different inhibitor concentrations are given in Table 2.

From Table 2, it can be concluded that the fact that β_c do not change markedly with inhibitors addition means that the inhibition of the hydrogen evolution reaction by benzodiazepine derivatives occurs by simple adsorption mode and the mechanism remains the same in inhibited and uninhibited media. A pronounced decrease in current density is registered with benzodiazepine at higher concentrations. It is circa six, eight and eleven times lower in the presence of BDZ1, BDZ2 and BZD3, respectively than the uninhibited solution. Consequently, the inhibition efficiency $E_I\%$ increases with inhibitor concentrations, reaching the values of 82 %, 87.4 % and 91.1 % at 10^{-3} M of BZD1, BZD2 and BZD3, respectively. The increase in inhibition efficiency observed at higher inhibitor concentrations is imputed to the fact that more inhibitor molecules are adsorbed on the metal surface thus providing wider surface coverage and these compounds are acting as adsorption inhibitors [18] by the creation of a barrier against infiltration of aggressive species to attain the mild steel/electrolyte interface.

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 BZD1, BZD2 and BZD3. Before each measurement, the electrode is left at the open circuit conditions during 1 h. The electrode system do not evolve significantly during the impedance measurements. The obtained impedance diagrams are characterized by one capacitive loop (Figure 2).

It is clear from these spectra that the impedance response of mild steel in the absence of inhibitors has significantly changed, in size, after the addition of BZD1, BZD2 and BZD3 into the corrosive medium. Indeed, the impedance of inhibited electrode increases with increasing inhibitor concentrations, and consequently the inhibition efficiency increases as it is explained hereafter.

A depressed semicircle, as often obtained in acidic media [19,20] can be seen. The difference from theoretical results is generally attributed to Cole-Cole [21,22] and/or Cole-Davidson [23] 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 [24,25], adsorption of inhibitors [26], and formation of porous layers [27,28]. The existence of single semicircle relates the presence of single charge transfer process, which is unaffected by the presence of BZD1, BZD2 and BZD3. According to a classical method, the EIS spectra of Figure 2 will be interpreted in terms of parallel R_t-C_{dl}□ circuit; i.e., one time constant τ_t.

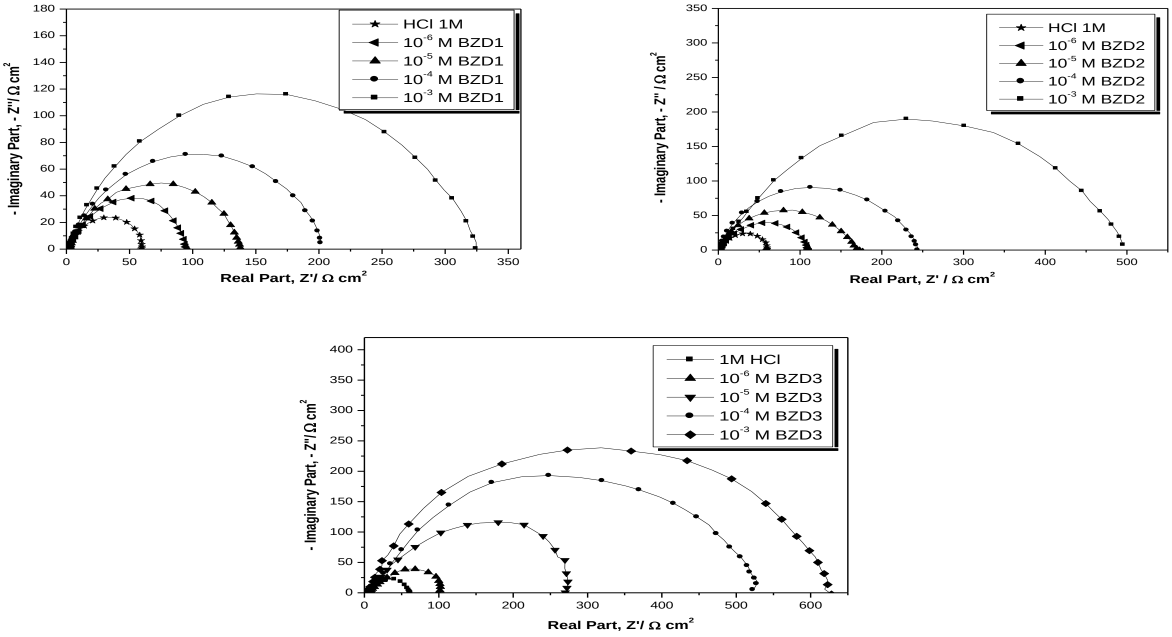


Figure 2. Nyquist diagrams for mild steel in 1M HCl without and with different concentrations of the undertaken inhibitors BZD1, BZD2 and BZD3.

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

Inhibitor	Concentration C / M	R_t Ω cm^2	f_{max} Hz	C_{dl} µF cm^{-2}	E_R %
Blank	00	60	20	133	—
BZD1	1 x 10^{-6}	96	12.5	132	37.5
	1 x 10^{-5}	145	10	109	58.6
	1 x 10^{-4}	200	7.93	100	70.0
	1 x 10^{-3}	325	6.32	75	81.5
BZD2	1 x 10^{-6}	110	12.5	115	45.5
	1 x 10^{-5}	175	7.93	114	65.7
	1 x 10^{-4}	245	10	65	75.5
	1 x 10^{-3}	495	5	64	87.9
BZD3	1 x 10^{-6}	100	12.5	127.4	40.0
	1 x 10^{-5}	260	25	24.5	76.9
	1 x 10^{-4}	450	20	17.6	86.6
	1 x 10^{-3}	630	15.8	15.9	90.5

Table 3 summarizes the impedance parameters at different concentrations of BZD1, BZD2 and BZD3 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_{dl}) is obtained at the frequency f_{max} on the apex of the imaginary component of the impedance $(-Z''_{\max})$ by equation 4:

$$f(-Z''_{\max}) = \frac{1}{2\pi\tau_t},\ where\ \tau_t = R_t C_{dl} \qquad (4)$$

From the impedance parameters, one can conclude that the value of R_t increases with concentration increase of BZD1, BZD2 and BZD3 which causes 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 benzodiazepine molecules and the decrease of C_{dl} 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_{dl} with rise in concentration of BZD1, BZD2 and BZD3 is in favour of their selectively adsorption in specific places and/or formation of complex onto the metal surface. According to this inhibition mechanism, BZD1, BZD2 and BZD3 can be adsorbed at active points causing the corrosion rate to drop. The value of inhibition efficiency obtained from EIS measurements for the tested inhibitors follows the order BZD3 > BZD2 > BZD1. The EIS results correspond to those obtained from polarization curves.

3.3. Weight loss measurements

The values of inhibition efficiency and corrosion rate obtained from weight loss method in the absence and presence of various concentrations of BZD1, BZD2 and BZD3 are given in Table 4. From these data, it is evident that for all studied inhibitors, the corrosion rate W_{corr} of mild steel decreases with increase of concentration and in turns the protection efficiency increases. The corrosion inhibition can be attributed to the adsorption of the studied inhibitors onto the mild steel surface. Maximum $E_W\%$ 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.

The variation in inhibiting efficiency mainly depends on the type and the nature of the substitution in the inhibitor molecule. The ability of a molecule to adsorb on the mild steel surface is dependent on the presence of sulphur atom (S) on BZD2 which arise an enhancement in the inhibiting efficiency when compared to BZD1 with oxygen atom (O). For BZD3, which presents beside sulphur atom a triazolic ring enhancing the molecular size, exhibits the best performance. 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. The same effect has been observed by Kissi et al. for the study of four organic compounds of pyrazine type [29]. The results obtained from the weight loss measurements are in agreement with those derived from linear polarization method and EIS measurements.

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

Inhibitor	Concentration C / M	Weight loss W_{corr} / mg cm^{-2} h^{-1}	E_W %	Surface coverage θ
Blank	00	1.15	–	
BZD1	$1 \text{ x } 10^{-6}$	0.90	21.7	0.217
	$1 \text{ x } 10^{-5}$	0.68	40.9	0.409
	5×10^{-5}	0.54	53.0	0.530
	$1 \text{ x } 10^{-4}$	0.39	66.1	0.661
	5×10^{-4}	0.24	79.1	0.791
	$1 \text{ x } 10^{-3}$	0.19	83.5	0.835
BZD2	$1 \text{ x } 10^{-6}$	0.81	29.6	0.296
	$1 \text{ x } 10^{-5}$	0.58	49.6	0.496
	5×10^{-5}	0.42	63.5	0.635
	$1 \text{ x } 10^{-4}$	0.33	71.3	0.713
	5×10^{-4}	0.19	83.5	0.835
	$1 \text{ x } 10^{-3}$	0.13	88.7	0.887
BZD3	$1 \text{ x } 10^{-6}$	0.70	39.2	0.392
	$1 \text{ x } 10^{-5}$	0.38	66.5	0.665
	5×10^{-5}	0.24	78.7	0.787
	$1 \text{ x } 10^{-4}$	0.21	82.0	0.820
	5×10^{-4}	0.12	89.6	0.896
	$1 \text{ x } 10^{-3}$	0.08	93.2	0.932

3.3.1 Effect of temperature

The temperature can modify the interaction between the mild steel electrode and the acidic medium in the absence and the presence of inhibitors. Weight loss measurements for mild steel in 1 M HCl at different concentrations of the best inhibitor BZD3, 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 BZD3, whereas very slow increase is registered in its presence. Therefore the values of inhibition efficiency of BZD3 remains circa constant with temperature increase at any explored concentration. The protective properties are very good even at 353 K and 10^{-3} M (91.8%). These results confirm that BZD3 acts as the best inhibitor in the range of the studied temperature. Thus BZD3 corrosion efficiency is then nearly temperature–independent. The corrosion reaction can be regarded as an Arrhenius-type process, equation 5 [30,31]:

$$W_{corr} = A\exp(-\frac{E_a}{RT}) \qquad (5)$$

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

The apparent activation energies E_a, at different concentrations of BZD3, are calculated by linear regression between lnW_{corr} and $1/T$ (Fig. 3) and the results are shown in Table 6. This last shows that the values of E_a, determined in the presence of BZD3, at different concentrations, are greater than the one 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 [33].

Table 5. Effect of temperature on corrosion rate of mild steel in 1 M HCl without and with BZD3 at different concentrations and the corresponding corrosion inhibition efficiencies

Temperature T / K	Concentration C / M	Weight loss W_{corr} / mg cm^{-2} h^{-1}	E_W %
313	00	1.30	–
	5 × 10^{-5}	0.33	74.6
	1 x 10^{-4}	0.23	82.3
	5 × 10^{-4}	0.14	89.2
	1 x 10^{-3}	0.09	93.1
323	00	3.47	–
	5 × 10^{-5}	0.68	80.4
	1 x 10^{-4}	0.54	84.4
	5 × 10^{-4}	0.32	90.8
	1 x 10^{-3}	0.2	94.2
333	00	6.72	–
	5 × 10^{-5}	1.63	75.7
	1 x 10^{-4}	1.07	84.1
	5 × 10^{-4}	0.65	90.3
	1 x 10^{-3}	0.39	94.1
343	00	10.8	–
	5 × 10^{-5}	2.68	75.2
	1 x 10^{-4}	1.98	81.7
	5 × 10^{-4}	1.16	89.3
	1 x 10^{-3}	0.76	93.0
353	00	19.2	–
	5 × 10^{-5}	5.17	73.1
	1 x 10^{-4}	3.89	79.8
	5 × 10^{-4}	2.08	89.2
	1 x 10^{-3}	1.58	91.8

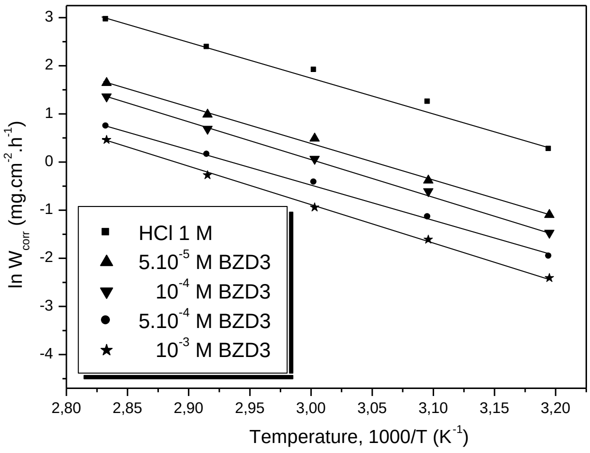


Figure 3. Arrhenius plots of lnW_{corr} versus $1/T$ at different concentrations of BZD3.

Table 6. Activation parameters E_a, ΔH^* and ΔS^* of mild steel dissolution in 1 M HCl in the absence and in the presence of BZD3 at different concentrations

Inhibitor	Concentration C / M	E_a kJ mol^{-1}	ΔH* kJ mol^{-1}	ΔS* J K^{-1} mol^{-1}
Blank	00	58.71	55.97	-62.94
BZD3	5×10^{-5}	63.0	60.5	-61.2
	$1 \text{ x } 10^{-4}$	63.4	62.2	-61.7
	5×10^{-4}	61.8	58.8	-73.5
	$1 \text{ x } 10^{-3}$	65.1	62.2	-66.9

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 BZD3 can provide further evidence [34,35] concerning the mechanism of the inhibiting action. The lower value of E_a in inhibited solution when compared to that for uninhibited one shows that strong chemisorption bond between the inhibitor and the metal is highly probable. In the opposite case a physisorption can usually occur. From Table 6, it appears that E_a values in inhibited media are slowly higher than the one in the blank solution. Hence, it can be suggested that the adsorption of BZD3 onto mild steel surface can involve both physisorption and chemisorption with large predominance of chemisorption. 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 (its d-submonolayer is incomplete) indicating chemisorption properties. Beside the fact that the inhibition phenomenon can be imputed to the presence of empty d-orbital in the Fe which led to an easier coordinate bond formation between the metal and inhibitors, these last contain sulphur, nitrogen and oxygen atoms which are easily protonated in HCl medium. Therefore, physical adsorption is also possible via electrostatic interaction between a negatively charged surface, which is provided with a specifically adsorbed chloride anion on mild steel, and the positive charge of the benzodiazepine molecules.

Activation parameters for the corrosion process are calculated using the alternative formulation of Arrhenius equation called transition state, equation 6 [32]:

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

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 activation enthalpy and the entropy activation of corrosion process, respectively.

Figure 4 shows the plots 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^*.

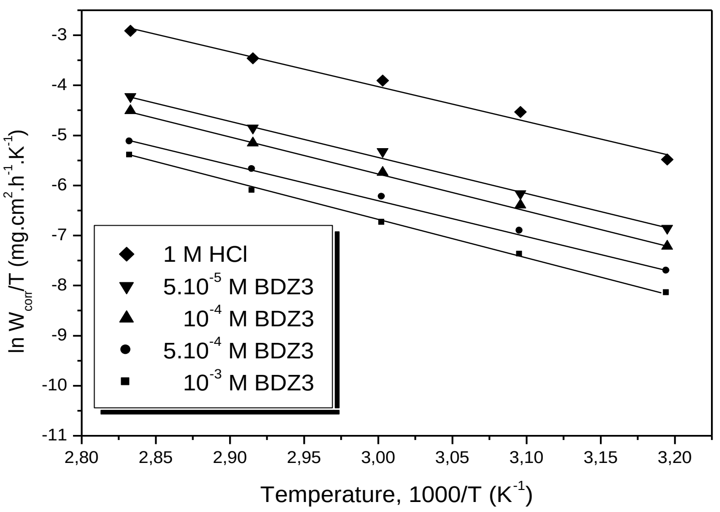


Figure 4. Arrhenius plots of lnW_{corr}/T versus $1/T$ at different concentrations of BZD3.

Inspection of curves (Fig. 4) and the values of ΔS^* and ΔH^* data in Table 6 reveals that the thermodynamic parameters ΔH^* of the dissolution reaction of mild steel in 1 M HCl in the presence of BZD3 are higher than that of in the absence of BZD3. The positive sign of the enthalpies ΔH^* reflects the endothermic nature of the steel dissolution process and means that the dissolution of steel is difficult [36]. Also, the entropy ΔS^* globally increases negatively with the presence of BZD3 than the non-inhibited one. This reflects the formation of an ordered stable layer of inhibitor on the steel surface [37] especially at both concentrations of 5 10^{-4} M and 10^{-3} M of BZD3.

3.3.2. 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 $\theta=E_W\%/100$, given in Table 4, increases with the inhibitor concentration; this is attributed to more adsorption of inhibitor molecules onto the steel surface. As it is known, the adsorption of an inhibitor is always a displacement reaction involving removal of absorbed water molecules from the metal surface as shown in equation 7 [38]:

$$\text{Org (sol)} + n\text{H}_2\text{O (ads)} = \text{Org (ads)} + n\text{H}_2\text{O (sol)} \qquad (7)$$

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 inhibitor.

Now, assuming that the adsorption of BZD3 belonged to monolayer adsorption, then the Langmuir adsorption isotherm is applied to investigate the mechanism by equation 8 [39]:

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

where K_{ads} is the adsorption coefficient and $\Delta_{ads}G°$ is the standard free energy of adsorption of BZD3.

The plots of C_{inh}/θ versus C_{inh} (Figure 5) with slopes around unity suggest that BZD3 adsorb on the metal surface obeying to the Langmuir's adsorption isotherm model. 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].

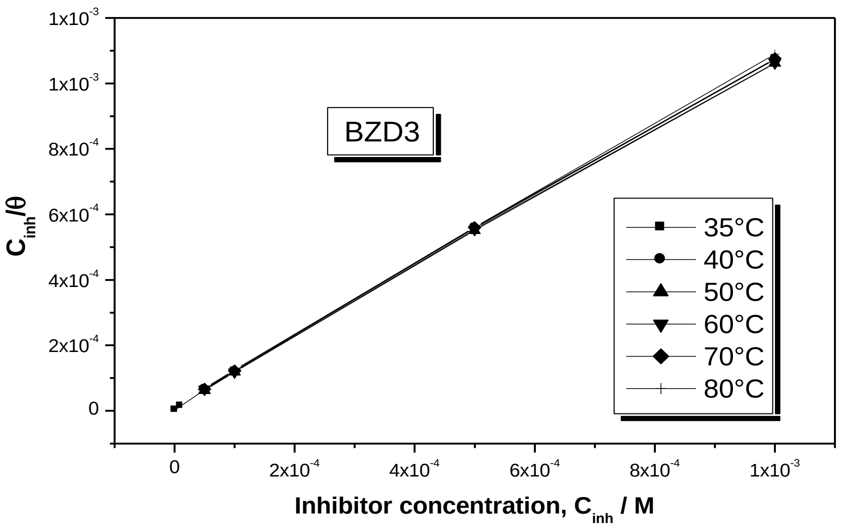


Figure 5. Langmuir isotherm adsorption model on the steel surface of BZD3 in 1 M HCl.

Table 7. Thermodynamic parameters for the adsorption of BZD3 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	63576	-39.3	-3.4	115
323	61697	-40.4		
333	59880	-41.6		
343	56657	-42.7		
353	56275	-43.9		

It is well known that the absolute values of $\Delta_{ads}G^0$ of order of 20 kJ mol^{-1} or lower indicate a physisorption; while those of order of 40 kJ mol^{-1} or higher are associated with chemisorption [9]. The obtained results of the standard Gibbs energies are -39.3 kJ.mol^{-1} at 313 K and -43.9 kJ mol^{-1} at 353 K (Table 7) for the experimental conditions of this work. The low and negative values of $\Delta_{ads}G°$ indicate the spontaneous adsorption of BZD3 on the mild steel surface. It is suggested that the adsorption mechanism of the investigated BZD3 on the mild steel surface in 1 M HCl solution involves two types of interaction; chemisorption and physisorption with mostly chemisorption.

Considering the values of standard enthalpy and standard entropy of the inhibition process have no distinct changes in the studied temperature range, the thermodynamic parameters $\Delta_{ads}H^\circ$ and $\Delta_{ads}S^\circ$ for the adsorption of BZD3 on mild steel can be calculated from the integrated version of the Vant'Hoff isobar expressed by equation 9 [42]:

$$\ln K_{ads} = -\frac{\Delta_{ads}H^\circ}{RT} + cte \qquad (9)$$

Figure 6 shows the plot of $\ln K_{ads}$ versus *1/T*. It gives straight line 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 10:

$$\Delta_{ads}G^\circ = \Delta_{ads}H^\circ - T\Delta_{ads}S^\circ \qquad (10)$$

The negative sign of $\Delta_{ads}H^\circ$ indicates that the adsorption of BZD3 molecules is an exothermic process. It is assumed that an exothermic process is attributed to either physical or chemical adsorption but endothermic process corresponds solely to chemisorption. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of $\Delta_{ads}H^\circ$. For a physisorption process $\Delta_{ads}H^\circ$, in absolute value, is lower than 40 kJ mol^{-1} while the adsorption heat of a chemisorption process approaches 100 kJ mol^{-1} [43]. In this study, the value of $\Delta_{ads}H^\circ$ is negative ($\Delta_{ads}H^\circ$=-3.4 kJ mol^{-1}), reflecting that the adsorption on the mild steel surface corresponds solely to chemisorption [44]. $\Delta_{ads}S^\circ$ in presence of BZD3 is large and positive meaning that an increase in disordering takes places in going from reactants to the metal-adsorbed species reaction complex [45].

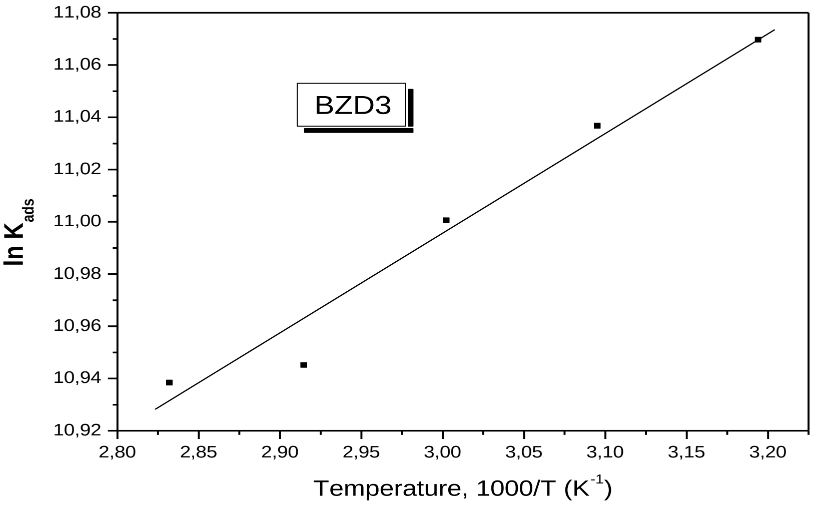


Figure 6. Vant'Hoff isobar plot for mild steel/BZD3 system in 1 M HCl.

4. CONCLUSIONS

* The studied benzodiazepine compounds show good inhibition properties for mild steel corrosion in 1 M HCl solutions.

* Potentiodynamic polarization measurements of BZD1 and BZD2 indicate that the studied inhibitors act predominantly as cathodic-type inhibitors which retarding both the cathodic process without changing the mechanism of corrosion process. But the presence of BZD3 decreases also the anodic current density versus potential characteristics, which indicates that BZD3 acts as mixed inhibitor.

* The inhibition efficiency of the studied inhibitors increased with inhibitor concentrations.

* The electrochemical impedance study shows that the use of BZD1, BZD2 and BZD3 significantly increases the charge transfer values and decreases the double layer capacitance in 1 M HCl, suggesting that the corrosion inhibition takes place by simple adsorption.

* The inhibition performance of BZD2 with sulphur heteroatom is found to be better than BZD1 with oxygen atom.

* The detailed study of BZD3 reflects that the values of inhibition efficiency remain constant despite the increase of temperature and the apparent activation energy of corrosion process increases very slightly with concentration increase when compared to the free solution. Besides, all values of the standard Gibbs energy of adsorption are negative and $|\Delta_{ads}G°|$ values are of ca. 40 kJ mol^{-1}. In addition, the value of standard heat enthalpy $\Delta_{ads}H°$ is of -3.4 kJ mol^{-1}. The consideration of the whole results is in favour of solely chemisorption of the adsorption mechanism of BZD3 onto mild steel surface.

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