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Thermodynamic and Adsorption Studies on the Corrosion Inhibition of Zn by 2, 2'-Dithiobis(2,3-dihydro-1,3-benzothiazole) in HCl Solutions

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Abstract

The thermodynamics parameters and adsorption mechanism of 2,2'-dithiobis(2,3-dihydro-1,3-benzothiazole), DDBT, as a corrosion inhibitor for zinc in 0.5 M HCl solution were studied by different techniques. The used organic compound was prepared in our lab by a transformation reaction for thiol compound in the presence of ammonium per-sulfate. Potentiodynamic polarization, thermometric and gravimetric techniques, as well as, scanning electron microscope, SEM surface investigations were employed. The data of different techniques were compatible and confirmed the inhibition effect of DDBT. The potentiodynamic polarization data disclosed that the DTDBT molecules behave as a mixed-kind inhibitor. The different thermodynamic parameters about the corrosion and adsorption processes such as E_a, ΔH_a, ΔS_a, $\Delta G°_{ads}$, $\Delta H°_{ads}$ and $\Delta S°_{ads}$ were deduced to suggest the inhibition mechanism. The DDBT molecules are adsorbed on the Zn surface confirming the Langmuir isotherm model obeying a mixed mechanism (physical and chemisorption).

Keywords: Transformation Synthesis, 2,2'-Dithiobis(2,3-dihydro-1,3-benzothiazole), Adsorption; Zinc; Corrosion inhibitor; Thermodynamic; Langmuir isotherm.

1. Introduction

The general use of Zinc is the steel galvanization for protection from corrosion processes and as anode for chloride and alkaline batteries. The economic benefits come from its high capacity (0.82Ah/g), rechargeable batteries, and high discharge efficiency [1-3]. Great efforts have been done by many scientists to use some active minerals such as zinc for producing hydrogen gas when the metal becomes in contact with acids [4-10]. The produced H_2, which accompanies the corrosion reactions as an individual cathodic reaction in the aqueous acidic solution was found to depend on many parameters such as inundation time, the strength of the acid, and the solution temperature. The produced H_2 gas delayed by the presence of the corrosion products formed on the metal surface or the corrosion inhibitors that reduce the contact surface area to the aggressive media [11].

The employing of organic corrosion inhibitors is considered a significant controller to reduce the deteriorative effect of acidic media. Generally, compounds that contain O, S, P, and N are considered as effective corrosion inhibitors [12-14]. Recent literature about such compounds confirms the importance of the inhibition against the corrosion of zinc in hydrochloric acid aqueous solutions [15-20]. Such molecules can form a film through the active sites on the metal surface via the formation of an adsorbed protective layer protecting the metal from the corrosive effect of the medium.

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Benzothiazole derivatives could be considered as one of the most important types of organic inhibitors. This is due to the presence of electronegative such as N and S atoms besides the π-electrons of aromatic rings, which is easy to adsorb on the metal to form a protective film. The mechanism of inhibition of such compounds was found to depend on the adsorption process on the metal surface as well as the inhibitor concentration and temperature. The efficient adsorption could have resulted from the presence of the π-electrons inside the selected molecule beside the unsaturated bonds formed in the presence of the heteroatoms (S or O or N) in the inhibitor's molecular composition [21].

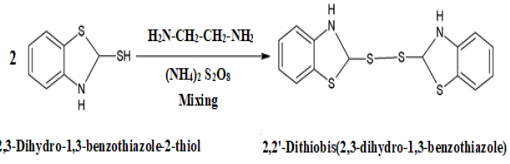
This study aimed to synthesize and evaluate the inhibition performance of dithiobis(2,3-dihydro-1,3-benzothiazole), DDBT, as an efficient retarder against the destruction of Zn in a 0.5 M HCl solutions. The material of DDBT is easily prepared in our laboratory with a high yield. The DDBT is easily soluble in dilute HCl and used as a corrosion inhibitor towards the H_2 gas production when Zn reacted with HCl solution. Chemical (gravimetric and thermometric) and electrochemical (Tafel) techniques, complemented by surface investigations using the SEM technique were used.

2-Experimental

2.1. Materials and electrolyte

2.1.1. Synthesis of DDBT inhibitor

The required inhibitor was prepared directly in the laboratory by a transformation reaction of thiol compound into disulfide by using ammonium persulfate in the presence of ethylenediamine [22]. The required amount of 2,3-dihydro-1,3-benzothiazole-2-thiol was weighed accurately in a mole unit (0.01 mole) and mixed thoroughly with the required amount of ethylenediamine (0.005 mole). The ammonium per-sulfate (0.011 mole) was added with continuous mixing using pestle and mortar for a while 40 min. After the accomplishment of the reaction, the crude product was extracted by using a dichloromethane solvent. The removal of the solvent under reduced pressure and the yield was recrystallized using ethanol. The synthetic route for the synthesis of 2,2'-dithiobis(2,3-dihydro-1,3-benzothiazole) (DDBT, inhibitor) is shown in scheme 1.



Scheme I. Synthetic route of 2,2'-dithiobis(2,3- ihydro-1,3-benzothiazole), DDBT.

2.1.2. Material

Zn sheet (Johnson- Matthey, UK) was prepared in suitable samples with dimensions 0.3 cm x 5cm x 2 cm for the gravimetric and thermometric measurements. For the polarization experiments, a zinc rod (working electrode) has the same chemical composition were entrenched in epoxy resin leaving an exposed surface area of 0.28 cm^2. The Zn sample was successively abraded with different grades of emery papers up to mirror finish. Then, it was washed with bi-distilled water, followed by rinsing with acetone, washed repeatedly with bi-distilled water, and finally immersed in the test solution. A fresh 0.5 M HCl solution was prepared using pure grade 37% HCl (BDH) and bi-distilled water. The inhibitor concentrations varied between 1.0 $x10^{-6}$ and $1x10^{-3}$ M freshly prepared in 0.5 M HCl before running the experiment. The substances of ethylenediamine, 2,3-dihydro-1,3-benzothiazole-2-thiol, and ammonium per-sulfate were obtained from Sigma-Aldrich Co., and Fluka Co., Germany chemicals.

2.2. Experimental techniques

The potentiodynamic polarization was carried on Volta lab 80 (PGZ 402) potentiostat with Volta master 4 software under static conditions. Three electrodes system with Zn rode as a working electrode, a saturated calomel electrode, SCE, as a reference electrode and Pt wire as a counter electrode. The potential/current curves were obtained by sweeping the electrode potential at 2 mVs^{-1} from $E_{initial}$ = -1220 mV to E_{final} = -800 mV.

The reaction vessel and the procedure of thermometric experiments for following the dissolution temperature of Zn in HCl have been described previously [12, 23-25]. The used thermometric vessel was made of Pyrex glass (Mylius tube) kept inside a Dewar flask to minimize heat exchange with the surrounding. The starting solution temperature in all experiments was kept at 26 °C and the rise in the temperature was pursued with time to ± 0.05 °C, using a calibrated thermometer (0–100 °C). The reaction number, R_N, can be deduced from the relation [12, 23-25]:

$$R_N = \left(\frac{T_m - T_i}{t}\right), °C\ min^{-1} \qquad (1)$$

where T_i and T_m are initial and maximum temperatures, respectively, while, t is the immersion time attained when the temperature reaches T_m.

The gravimetric method was similar to that reported earlier [12, 23-25]. The mass of a clean polished Zn sample was determined before (m_1) and after (m_2) immersion in the test solution, for the desired time. The weight of each sample was determined using an analytical balance (precision ± 0.001g). Each run was duplicated and the average mass loss was determined from the difference between m_2 and m_1 ($\Delta m = m_1 - m_2$). The rate of the reaction, r_{corr}, expressed in mg cm^{-2} min^{-1} was calculated by using the following equation:

$$r_{corr} = \frac{\Delta m}{At} \qquad (2)$$

where A is the total surface area of the Zn sample, and t is the immersion time. The surface coverage, θ, and the inhibition efficiency, η_w %, were calculated, respectively, from r_{corr} values using the following equations:

$$\theta = \left(1 - \frac{r_{corr}}{r^{\circ}_{corr}}\right) \qquad (3)$$

$$\eta_w = 100\,(\theta) \qquad (4)$$

where r^{o}_{corr} and r_{corr} are the rates of corrosion reaction in 0.5 M HCl in the absence and presence of the DDBT inhibitor, respectively.

2.3. Surface characterization analysis

The zinc specimens of size 1 cm × 1 cm were prepared as described above. The scanning electron microscope is used to investigate the surface morphology of some of the corroded Zn samples. The investigated samples were used before and after immersion for three hours in 0.5 M HCl without and with $1x10^{-4}$ M DDBT inhibitor. The working instrument was A Jeol type, JSM-5410 (Japan), has an accelerated voltage of 25 kV with a working distance of 20 mm.

3. Results and discussion

3.1. Polarization study.

The anodic and cathodic potentiodynamic polarization curves of Zn in 0.5 M HCl without and with various additions of DDBT are plotted in Fig. 1, at 25 °C. It is cleared that, the cathodic and anodic curves are shifted to less active direction by the presence of different additives of DDBT due to the increase in the overvoltage accompanying the cathodic and anodic processes. Such behavior could prove that the mechanism of Zn dissolution and H_2 evolution is under an activation-controlled process, and not altered by the presence of DDBT inhibitor [26, 27].

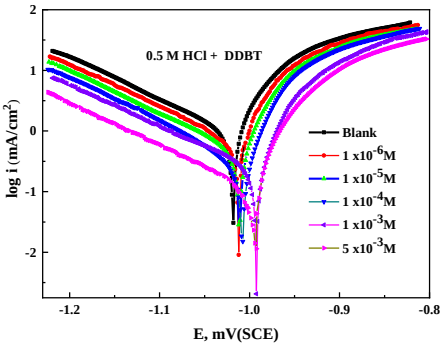


Fig 1. The potentiodynamic polarization curves of for Zn in 0.5 M HCl solution devoid of and containing different additions of DDBT inhibitor.

The surface coverage, θ, and the inhibition efficiency η_p %, are determined using the following relations [26-30].

$$\theta = \left(\frac{I^{\circ}_{corr} - I_{corr}}{I^{\circ}_{corr}}\right) \qquad (5)$$

$$\eta_p = \left(\frac{I^{\circ}_{corr} - I_{corr}}{I^{\circ}_{corr}}\right) 100 \qquad (6)$$

where, $I°_{corr}$ and I_{corr} are the uninhibited and inhibited corrosion current densities of Zn in 0.5 M HCl, respectively. Table 1 displayed the electrochemical corrosion parameters, viz., corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic (β_a), cathodic (β_c) Tafel slopes, surface coverage, θ, the percentage of inhibition efficiency (η_p %) and the standard deviation, σ. Inspection of the data of Table 1 reveals that, both the values of θ and η_p % increase with increasing the inhibitor concentration. The increase in the DDBT concentration is accompanied by the reduction in the corrosion current density (I_{corr}) with a corresponding increase in the values of θ and η_p %.

Table 1: The polarization parameters (E_{corr}, β_a, β_c, I_{corr}, θ and η_p %) and the standard deviation, σ, corresponding the inhibition efficacy, for Zn corrosion in 0.5 M HCl containing different concentrations of DDBT inhibitor, at 25°C.

Conc., M	$-E_{corr}$, mV	β_a, mV/dec	$-\beta_c$, mV/dec	I_{corr}, mAcm^{-2}	θ	η_p %	Standard deviation, σ,
Free acid	1017	42	131	0.79	--	--	
1 x 10^{-6}	1013	43	141	0.45	0.423	42.31	8.8
1x 10^{-5}	1011	39	136	0.34	0.564	56.41	3.5
1 x 10^{-4}	1007	38	130	0.29	0.628	62.82	8.4
5 x 10^{-4}	993	35	165	0.21	0.731	73.08	6.4
1 x 10^{-3}	990	37	167	0.15	0.821	82.05	6.6

Table 2: The values of the reaction number, R_N, surface coverage, θ, and the inhibition efficiency, η_R %, for the corrosion of Zn in 0.5 M HCl in the presence of different concentrations of DDBT inhibitor.

Concentration	R_N, $^oC.min^{-1}$	θ	η_R %
Free acid	1.948	--	
1 x 10^{-6} M	1.469	0.246	24.6
5 x 10^{-6} M	1.110	0.430	43.5
1 x 10^{-5} M	0.745	0.618	61.8
1 x 10^{-4} M	0.397	0.796	79.6
5 x 10^{-4} M	0.196	0.899	89.9
1 x 10^{-3} M	0.103	0.947	94.7

The values of η_p % for the different concentrations of the DDBT inhibitor, obtained by the three different experimental techniques, potentiodynamic polarization, thermometric and gravimetric techniques are collected in Tables 1 and 2. The standard deviation values, σ, of the inhibitory efficiencies calculated by the three techniques are included in Table 1. The σ values were varied between 3.5 and 8.8, depending on the inhibitor concentration, which confirms the good agreement between the used techniques. The relatively high values of σ could be attributed to the difference in the acid concentration with the thermometric method (1.0 M HCl) than other methods (0.5 M HCl) besides the experimental conditions of each technique.

Also, the non-significant changes in the values of β_a and β_c, besides the little displacement in E_{corr} (4-27 mVSCE), which less than 85 mV, confirm that the used inhibitor is considered as a mixed-type inhibitor [31-36].

3.2. Thermometric study

The effect of the addition of DDBT inhibitor on the corrosion of zinc in 1.0 M HCl solution was investigated by the thermometric technique. Fig 2 depicts the temperature-time relations for Zn in 1.0 M HCl solution devoid of and containing different additions of DDBT inhibitor. The presence of DDBT inhibitor decreases the reaction number, R_N (Table 2) through a decrease in T_m and an elongation of the time, t needed to attain T_m. This behavior is due to the retardation in the corrosion reaction, the R_N values are used to express the rate of reaction in the free acid and inhibitive solutions.

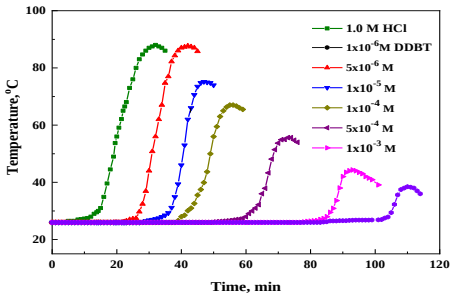


Fig 2. Variation of the temperature with the immersion time for Zn in 1.0 M HCl solution devoid of and containing different additions of DDBT.

Table 3: Different gravimetric data for the corrosion of Zn in 0.5 M HCl in the absence and presence of different concentrations of DDBT inhibitor, at different temperatures.

T, k	Parameter	Free acid	$1x10^{-6}$ M	$1x10^{-5}$ M	$1x10^{-4}$ M	$1x10^{-3}$ M
298	r_{corr}, µg $cm^{-2}.min^{-1}$	2.543	1.655	1.142	0.478	0.210
	θ	--	0.349	0.551	0.808	0.917
	η_W %	--	34.90	55.10	80.80	91.70
303	r_{corr}, µg $cm^{-2}.min^{-1}$	2.745	1.921	1.395	0.825	0.345
	θ	--	0.300	0.492	0.768	0.873
	η_W %	--	30.00	49.20	76.80	87.30
308	r_{corr}, µg $cm^{-2}.min^{-1}$	2.957	2.215	1.712	0.869	0.470
	θ	--	0.251	0.421	0.706	0.841
	η_W %	--	25.10	42.10	70.60	84.10
313	r_{corr}, µg $cm^{-2}.min^{-1}$	3.177	2.571	2.083	1.083	0.799
	θ	--	0.191	0.344	0.659	0.749
	η_W %	--	19.10	34.40	65.90	74.85
318	r_{corr}, µg $cm^{-2}.min^{-1}$	3.385	2.942	2.356	1.441	0.951
	θ	--	0.131	0.304	0.574	0.719
	η_W %	--	13.10	30.40	57.40	71.91

A plot of the reaction number, R_N, as a function of the logarithm of the molar concentration of the added DDBT inhibitor, gives a sigmoidal S-shaped curve, Fig 3, which confirms the presence of an adsorption step [12, 24]. It is cleared that increasing the DDBT inhibitor concentration reduces the R_N values, lowering the corrosion rate due to the adsorption of the inhibitor molecules on the Zn surface producing a protective film.

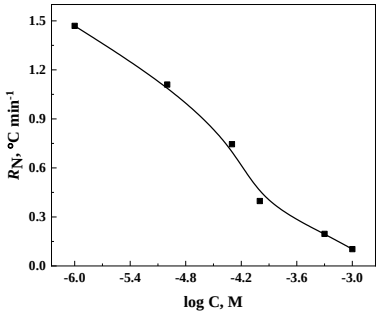


Fig 3. Variation of the reaction number, R_N, as a function of the logarithm of the molar concentration of the added DDBT inhibitor.

The R_N values at different additions of DDBT inhibitor are used to calculate the surface coverage, θ, and the inhibition efficiency, η_N, according to the following equation [12, 24, 25]:

$$\theta = \left(1 - \frac{R_N}{R_N^\circ}\right) \quad (7)$$

$$\eta_N = \left(1 - \frac{R_N}{R_N^\circ}\right) 100 \quad (8)$$

where $R°_N$ and R_N are the reaction numbers in the absence and presence of the DDBT inhibitor, respectively. The values of θ and η_N, of the DDBT inhibitor, are listed in Table 2. The data reveals that the values of θ and η_N are increased as the inhibitor concentration is increased confirming the inhibition of Zn corrosion in 1.0 M HCl, which is consistent with the data obtained by other used techniques.

3.3. Gravimetric study

The gravimetric study is used to confirm the inhibition effect on the corrosion of Zn in 0.5 M HCl when different additions of DDBT inhibitor, at various temperatures. The data are used to determine the different corrosion parameters such as corrosion rate, r_{corr} (mg/cm^2/h), θ and η_w, Table 3. Fig 4 depicts the variation in the corrosion reaction rate, r_{corr}, with the logarithm of the molar concentration of the added DDBT inhibitor. It is clear that the rate of reaction, r_{corr}, raises with the temperature in the case of the free and the inhibited solutions, although it decreases as the inhibitor concentration is raised, at a fixed temperature. The higher additions of DDBT inhibitor cause more lowering in the corrosion rate and gives high values for the surface coverage, θ, and the inhibition efficacy, η_w, Table 3. The sigmoid nature of η_w - log C_{inh} curves, of Fig 4 could confirm the adsorptive ability of the DDBT inhibitor towards the Zn metal surface [12]. The decrease in the inhibition efficiency values, η_w, for the DDBT inhibitor at high temperature (Fig 4) could be related to the desorption of some of the DDBT molecules with the rise in the temperature [37].

Table 4: Adsorption parameters for DDBT inhibitor on the Zn surface in 0.5 M HCl, obtained from Langmuir adsorption isotherm at different temperatures

T, K	R^2	K_{ads},	ΔG^o_{ads},	ΔH^o_{ads},	ΔS^o_{ads},
		M^{-1}	kJ/mol	kJ mol^{-1}	J mol^{-1} K^{-1}
298	0.9998	$11.03x10^4$	38.72		332
303	0.9997	$7.11x10^4$	38.26		325
308	0.9999	$3.85x10^4$	38.12	60.19	319
313	0.9997	$3.27x10^4$	37.50		312
318	0.9988	$2.43x10^4$	37.31		307

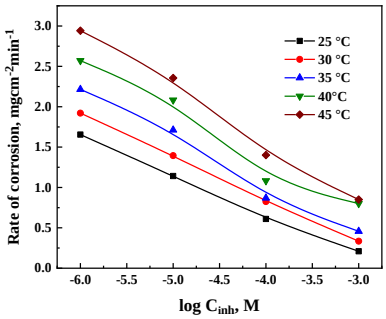


Fig 4. Variation of the corrosion reaction rate, r_{corr}, as a function of the logarithm of the molar concentration of the added DDBT inhibitor.

Furthermore, comparison and validation of the obtained results, inhibition efficiency, is an important phase of search studies. Besides, the variation of inhibition efficiency η (%) gained by the three experimental techniques used in this study, as a function of DDBT concentration in 0.5 M HCl is presented in Tables1-3.

3.4. Adsorption behaviour

The adsorption of the organic inhibitors on the investigated metal surface in aggressive aqueous solutions can be attributed to the presence of lone pair of electrons on the heteroatoms of the inhibitor molecules. Adsorption of inhibitor is considered a substitution process in which an exchange between adsorbed H_2O molecules and organic molecules takes place.

The surface coverage, θ, calculated from the data of gravimetric measurements is used as a function of the used inhibitor concentration, to scrutinize the type of adsorption isotherm. The isotherm accounts for the nature of the interaction between the inhibitor molecules and the metal. In this investigation, the best-fit isotherm was the Langmuir model. The applicable isotherm can be achieved from the relation [38, 39]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (9)$$

The plotting of C_{inh}/θ vs C_{inh}, at different temperatures, give straight lines, as shown in Fig 6. The values of the slope and r are approximately equal to one, which confirms the adsorption of DDBT on the Zn surface according to the Langmuir's isotherm. The corresponding linear regression coefficient (r^2), and the adsorption equilibrium constant, K_{ads} are collected in Table 4. High values of K_{ads} for studied inhibitor reflect strong interaction of DDBT with Zn surface [40] confirming strong adsorption of DDBT on the metal surface in 0.5 M HCl. The depress in K_{ads} values with temperature (Table 4) indicates a drop in the adsorptive ability due to the desorption of DDBT molecules on the Zn surface [41].

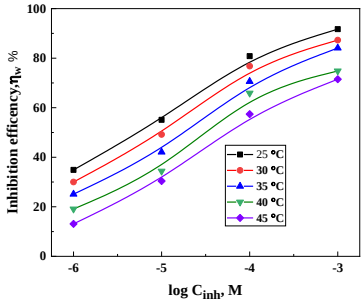


Fig 5. Variation of the inhibition efficiency, η_w, as a function of the logarithm of the molar concentration of the added DDBT inhibitor.

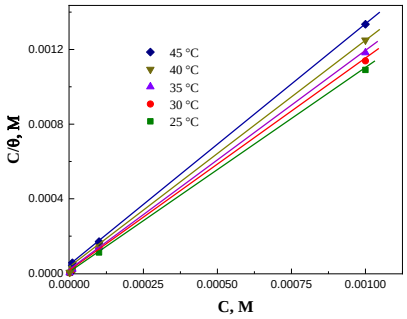


Fig 6. Langmuir adsorption isotherm for DDBT inhibitor on the Zn surface in 0.5 M HCl at different temperatures.

3.5. Adsorption thermodynamic parameters

The equilibrium constant for the adsorption process, K_{ads} is used to calculate the standard free energy of adsorption, $\Delta G°_{ads}$, using the equation [42]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta \breve{G}_{ads}}{RT}\right) \qquad (10)$$

where 55.5 is the molar concentration value of H_2O in mol/L and R is the universal gas constant. The calculated values of $\Delta G°_{ads}$ are recorded in Table 4. The negative sign of $\Delta G°_{ads}$ secures the spontaneity of the adsorption process and fastness of the adsorbed DDBT film on the Zn surface. When $\Delta G°_{ads}$ values around -40 kJ mol^{-1} or more negative allude to the chemisorption type, while those around -20 kJ mol^{-1} or less negative are correlating to physical adsorption [43, 44]. In our case, the calculated values of $\Delta G°_{ads}$ (Table 6) were -38.72, 38.26, -38.12, -37.50 and - 37.31 kJ mol^{-1} at 25, 30, 35, 40, 45°C, respectively. These values confirm that a mixed chemi and physisorption is involved in the inhibition process [45, 46].

Adsorption thermodynamic parameters are employed to elucidate the adsorption behaviour of DDBT on the Zn surface. The standard enthalpy of adsorption ($\Delta H°_{ads}$) can be calculated from the Van't Hoff equation [40].

$$\frac{d \ln K_{ads}}{dT} = \frac{\Delta \breve{H}^{o}_{ads}}{RT^2} \qquad (11)$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the absolute temperature (K). The indefinite integration of equation 11 can give [45]:

$$\ln K_{ads} = -\left(\frac{\Delta \breve{H}_{ads}}{RT}\right) + \text{constant} \qquad (12)$$

The values of ln K_{ads} are plotted against 1/T, Fig 7, to give a straight-line relation, with a slope equal to - $\Delta H°_{ads}$/R. The value of $\Delta H°_{ads}$ is found to be -60.19 kJ/mol, Table 4. It has been reported that the endothermic adsorption process ($\Delta H°_{ads} > 0$) is accompanied to chemisorption process, while the exothermic adsorption process ($\Delta H°_{ads} < 0$) may be attributed to physisorption, chemisorption, or a mixture of both adsorption processes [46]. The negative sign of the obtained $\Delta H°_{ads}$ indicates the exothermic nature of adsorption of DDBT on the Zn surface in 0.5 M HCl. From the other side, the value of enthalpy is < 100 kJ mol^{-1}, which announces that the adsorption of DDBT on Zn surface is not merely physical or chemical, but the mixed type [38, 40]. . For the chemisorption process, $\Delta H°_{ads}$ approaches 100 kJ mol^{-1}, while for the physisorption process, it is less than 40 kJ mol^{-1} [47].

Table 5: Activation parameters of dissolution reaction of Zn in 0.5 M HCl containing different concentrations of DDBT inhibitor.

Conc, M	E_a, kJ mol^{-1}	ΔH_a, kJ mol^{-1}	$-\Delta S_a$, J mol^{-1}
Free	11.35	10.5	208
1x10^{-6} M	22.73	20.2	173
1x10^{-5} M	31.02	28.4	149
1x10^{-4} M	32.33	34.9	133
1x10^{-3} M	68.98	66.4	035

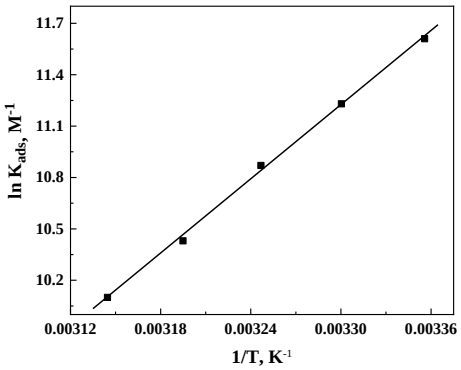


Fig 7. Van't Hoff plot for zinc in 0.5 M HCl with DDBT inhibitor.

The standard adsorption of entropy, $\Delta S°_{ads}$, can also obtain from the following equation [46, 48]:

$$\Delta S^{o}_{ads} = \frac{\Delta H^{o}_{ads} - \Delta G^{o}_{ads}}{T} \qquad (13)$$

The values of $\Delta S°_{ads}$ can be calculated and collected in Table 4. The positive values of $\Delta S°_{ads}$ suggest that adsorption is accompanied by an increase in the disorder system due to the adsorption of inhibitor molecules on the Zn surface [49].

3.6. Effect of temperature

The effect of temperature on the corrosion of Zn was further examined at different temperatures (298 – 338 K) to explore and deduce the activation corrosion parameters in the 0.5 M HCl in the absence and presence of different concentrations of DDBT inhibitor. The values of r_{corr} are found to increase with the raise the temperature, in the case of the free acid and the inhibitive solutions. Temperature enhances the rate of diffusion of H^+ ions to the metal surface, as well as the ionic mobility [12, 43]. The decrease in r_{corr} values, in the case of inhibitor, confirms the decrease in each of the anodic metal dissolution and the corresponding cathodic H_2 production, without altering the mechanism of the reaction.

The required apparent activation energy, E_a, can be calculated using Arrhenius equation [38, 50]:

$$r_{corr} = A \exp\left(\frac{-E_a}{RT}\right) \qquad (14)$$

where r_{corr} is the rate of corrosion reaction calculated by the gravimetric method, A represents the Arrhenius factor, T is the absolute temperature and R = 8.314J mol-1 is the universal gas constant.

However, the values of E_a can be determined mathematically from the Arrhenius graph, Fig 8 (variation of log r_{corr} against T^{-1}), and are given in Table 5. The obtained value of E_a for Zn in the blank solution is 11.35 kJ/mol. In the presence of different concentrations of DDBT, E_a varied between 22.73 and 68.98 kJ/mol depending on the inhibitor concentration. The increase in activation energy E_a in presence of DDBT indicates that the retardation in the corrosion rate is controlled by the adsorption of the inhibitor on the Zn surface [51, 52]. Moreover, the increase in E_a with the inhibitor is often supporting the physical adsorption mechanism [53].

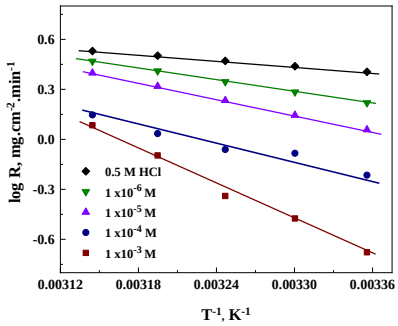


Fig 8. Arrhenius plots for the corrosion rate of Zn in 0.5 M HCl in absence and in presence of different concentrations of DDBT.

The values of r_{corr} ($mgcm^{-2}min^{-1}$) at different temperatures are used to locate the values of apparent enthalpy of activation ΔH_a and apparent entropy of activation ΔS_a for the formation of the activation complex, using transition state equation [37, 50–52]:

$$r_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right) \qquad (15)$$

where h is Planck's constant and N is the Avogadro's number. From the linear plot of log (r_{corr}/T) vs T^{-1}, Fig 9, ΔH_a and ΔS_a were calculated using the slope

and the intercept, successively, obtained by the linear fit, Table 5. The positive sign of ΔH_a reflects the endothermic nature of Zn dissolution in the absence and presence of inhibitor. The increase in the values of ΔHa in presence of DDBT means that the dissolution of Zn becomes more difficult in the presence of the inhibitor [53]. The negative value of ΔS_a (Table 4) indicates that the activated complex in the rate-determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the transition from reactant to the activated complex [54]

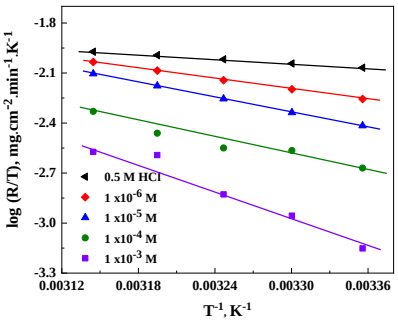


Fig 9. Transition-state plots for the corrosion rate of Zn in 0.5 M HCl in absence and in presence of different concentrations of DDBT.

3.7. Surface morphology.

The surface investigation has been carried out to Zn surfaces to understand the surface properties and morphology during the electrochemical corrosion behaviour. Figs 10 (A, B) show the SEM micrographs after immersion for 3 hr in 0.5 M HCl solution (A) without inhibitor and (B) with 1x 10^{-5} M DDBT, at 25 °C. The SEM micrograph of the corroded Zn sample in 0.5 M HCl solution (10A) shows a uniform damaged Zn surface covered by corrosion products. The large corroded areas might probably have been formed from smaller pits expanded equally laterally, as well as, inwardly so that it takes the shape of large attacked areas. In contrast, in the presence of the inhibitor, less damage surface with little numbers of pits can be seen on the zinc surface (10B). Therefore, the presence of the inhibitor decreased the rate of corrosion Zn in 0.5 M HCl.

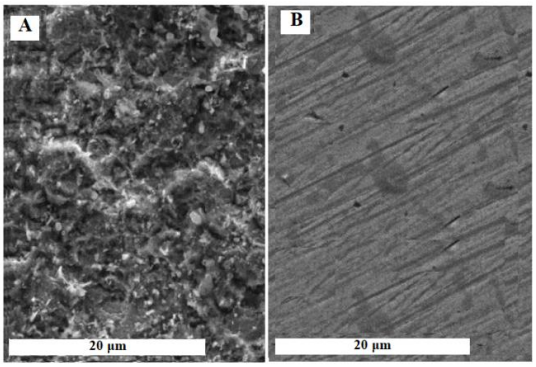


Fig 10. The SEM micrographs for Zn surface after immersion for 3hr in (A) 0.5 M HCl and (B) 0.5 M HCl containing 1 x10^{-4} M DDBT inhibitor, at 25 °C.

3.8. Inhibition mechanism

The corrosion protection of Zn by 2,2'-dithiobis(2,3-dihydro-1,3-benzothiazole), DDBT is attributed to the adsorption through the active sites on the metallic surface (Zn/HCl interface) to form a protective film. The adsorption of this inhibitor is facilitated by the presence of heteroatoms of N and S on the inhibitor molecule with lone pairs of free electrons beside the electrons of two benzene rings already included in the molecule. The formed film isolates the metal surface from the aggressive medium preventing direct contact with the aggressive acid. The adsorption of DDBT molecules at Zn/HCl water interface can be regarded as a replacement process between DDBT molecules in the aqueous solution, $DDBT_{aq}$, and water molecules on the Zn surface, H_2O_{ads}

$$DDBT_{aq} + x\ H_2O_{ads} \leftrightarrow DDBT_{ads} + x\ H_2O_{aq} \quad (16)$$

where x is the number of water molecules replaced by a molecule of $DDBT_{ads}$. $DDBT_{ads}$ molecules can adsorb on the Zn surface via the lone pair of free electrons located on the N and S atoms without ignoring the effective conjugated role of the π-electrons system in the molecule [8, 9].

From the second point of view, a protonated inhibitor species $DDBTH^+_{ads}$ is easily formed in the acidic medium. The formed $DDBTH^+_{ads}$ charged molecules electrostatically interact with $ZnCl^-_{ads}$, so the oxidation of Zn to form $ZnCl_2$ can be prevented. Also, since the discharge of H^+ ions to form adsorbed H atoms on the Zn surface is the rate-determining

step, the adsorption of efficient $DDBT_{ads}$ molecules will almost cover the surface leading to retardation of discharge of H^+ ions [9].

At lower concentrations of the adsorbed inhibitor, the formed Zn $DDBTH_{ads}$ is more soluble and its concentration is not enough to cover the Zn surface. Therefore, the corrosion process takes place on the sites free from Zn $DDBTH_{ads}$. When $DDBTH_{sol}$ concentration is high enough, a compact and coherent inhibitor layer is formed on the Zn surface, reducing the corrosion process.

4. Conclusions

1. The rate of H_2 production increases with the immersion time and the solution temperature.

2. Small additions of 2,2'-dithiobis(2,3-dihydro-1,3-benzothiazole), DDBT decrease the corrosion rate as confirmed from the data of Tafel and EIS techniques.

3. Polarization data indicate that 2,2'-dithiobis(2,3-dihydro-1,3-benzothiazole), DDBT is a mixed inhibitor.

4. The inhibition efficiency is increased with increasing inhibitor concentration and a decrease with the temperature.

5. The adsorption process is mixed between physical and chemical processes according to Langmuir isotherm.

6. The adsorption process is mixed between physical and chemical processes according to Langmuir isotherm.

5. Conflicts of interest

There are no conflicts to declare.

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