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Original scientific paper

Experimental study and mathematical modeling of the corrosion inhibition of mild steel with an organic compound in 1 M HCl

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Abstract

In this paper, a synthesized organic compound from the family of ketene dithioacetal was studied as corrosion inhibitor for mild steel in 1.0 M hydrochloric acid by gravimetric measurements. The aim of this work is to study the effect of inhibitor concentration and temperature on the corrosion resistance, and to compare the experimental results with those obtained by mathematical models. The structural properties are characterized using the scanning electron microscopy technique. It has been found that the inhibition efficiency increases with increasing inhibitor concentration. The adsorption of studied compound on mild steel surface follows Langmuir's isotherm. Taking into account the influence of inhibitor concentration and temperature on the corrosion inhibition efficiency, obtained data were analyzed by two mathematical models based on linear and quadratic regression. The obtained experimental results are in a good agreement with those predicted by the quadratic regression models.

Keywords

Ketene dithioacetal; hydrochloric acid; gravimetric measurements; linear regression; quadratic regression.

Introduction

The use of organic inhibitors for the control of corrosion of metals and alloys is of practical importance for many industrial applications, where acid solutions are commonly used in several processes. Among these, hydrochloric acid is one of the most widely used for pickling, and chemical and electrochemical etching of some metals and alloys [1]. Because of acid aggressiveness, the use of corrosion inhibitors is considered as the most effective method for the protection of many metals and alloys against acid attack [2-7]. Inhibitors are also employed to reduce the dissolution rate of metals.

Many authors have reported various types of organic inhibitors used as corrosion inhibitors for steel in hydrochloric acid solution [8-15]. These investigations revealed that organic compounds are acting as inhibitors due to heteroatoms such as nitrogen, sulfur, oxygen and phosphorus, which owing to their free electron pairs are capable to form coordinate covalent bonds with metals. In addition, π electrons in triple or conjugated double bond also exhibit good inhibitive properties [16-18].

The purpose of this work is to investigate the inhibitory action of the organic compound 1,3-dithianes, substituted with two electroactive groups A1 and A2: 3-(1,3-dithian-2-ylidene) pentane-2,4 dione (PDDY). The behavior of mild steel in acidic medium in the absence and presence of the inhibitor at different concentrations (5×10^{-6} - 10^{-3} M) and at various temperatures (20-60 °C) was explored. The chemical structure of PDDY is shown in Figure 1. The assessment of corrosion behavior is carried out using weight loss measurements and scanning electron micrograph (SEM) imaging at 20 °C. In the second part of this work, two mathematical models, based on linear and quadratic regression, are suggested to investigate the effect of concentration and temperature upon inhibition efficiency of PDDY.

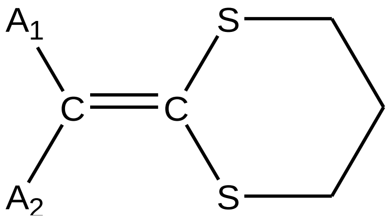

Figure 1. *Chemical structure of 3-(1, 3-dithian-2-ylidene) pentane-2,4 dione compound (PDDY)*

Experimental

Preparation of samples

The composition of mild steel used in this study is: C - 0.09 wt.%; Si - 0.05 wt.%; Mn - 0.13 wt.%; S - 0.24 wt.%; P - 0.24 wt.% and Fe balance. The mild steel specimens were cut into 1 × 1 × 1 cm pieces for the mass measurements. The specimens were abraded with a series of SiC papers (grades 320, 400, 500, 800, 1000, 1200 and 2000), washed with distilled water, degreased with acetone, and dried with a cold air stream at room temperature before use in the experiments.

Electrolytic solution

The aqueous electrolyte solution (1 M HCl) was prepared by dilution of analytical reagent grade, 37 % w/w HCl (Merck) with bi-distilled water. The measurements were carried out in 1 M HCl in the absence and presence of the inhibitor within the concentration range 5×10^{-6} to 1×10^{-3} M.

Preparation of inhibitor

The inhibitor 3-(1,3-dithian-2-ylidene) pentane-2,4-dione was synthesized using K_2CO_3 (21 g, 0.15 mol) and active methylene compound, 5.2 ml (0.05 mol) in 25 ml of DMF. The mixture was stirred magnetically. 4.5 mL (0.075 mol) of carbon disulfide was then added in just one time at room temperature. The stirring was maintained for 10 min before dropwise addition of reagent dielectrophile, 7.2 ml (0.06 mol) 1,3-dibromopropane, during 20 min. After seven hours of stirring at room temperature, 250 mL of ice water was added to the reaction mixture. The formed precipitate was filtered, dried and then purified by recrystallization from ethanol and used directly in the experiments in the concentration range (5×10^{-6}, 10^{-5}, 5×10^{-5}, 10^{-4}, 5×10^{-4} and 10^{-3}) mol L^{-1} [19]. The studied compound was recovered in the form of orange crystals, exhibiting the following characteristics: molar mass, M = 216 g/mol, yield 83 %, M.P. =104 °C. FT-IR (FT-IR spectra of PDDY in its solid state, $1/\lambda$: 1630 cm^{-1} (C=O), 1725 cm^{-1} (H_3C-C=O), 1173-1234 cm^{-1} (C-S-C), 1415 cm^{-1} (C=C). ^{1}H NMR (($CDCl_3$), 250 MHz)): δ = 2.32 ppm (s, 6H, $2CH_3$), δ = 2.25 ppm (m, 2H, CH_2), δ = 2.95 ppm (t, 4H, $2CH_2$). The mass spectroscopy analysis revealed that the inhibitor produced fragment ions m/z 217.

Scanning electron microscopy (SEM)

The morphological structures of mild steel surfaces before and after total immersion for 3 h in a corrosive solution (1 M HCl) with and without addition of 10^{-3} M of PDDY at 20 °C, were determined by the scanning electron microscope, model JEOL JSM-6360 LV.

Gravimetric measurements

Gravimetric experiments were performed according to the standard methods [20-22]. Experiments were conducted under total immersion of mild steel specimens in the stagnant and aerated conditions, using 250 mL capacity beakers. After being weighed accurately with high sensitivity balance, the specimens were immersed in 100 mL of 1 M HCl with and without various concentrations (5×10^{-6} - 10^{-3} M) of PDDY at various temperatures (20, 30, 40, 50 and 60 °C) in aerated conditions. After 3 hours of immersion, the specimens were taken out, rinsed thoroughly with distilled water, dried and weighed accurately again. The average of three replicates was used to further process the data. The average weight loss ΔW was calculated using the equation (1):

$$\Delta W = W_1 - W_2 \tag{1}$$

where, W_1 and W_2 are respectively the average weight of specimens before and after immersion. The corrosion rate (CR) in mg cm^{-2} h^{-1}, the surface coverage (θ) and inhibition efficiency (IE_W), obtained from gravimetric experiments were computed using the equations (2)-(4) [20,23,24]:

$$\mathrm{CR} = \frac{\Delta W}{St} \tag{2}$$

$$\theta = \frac{\mathrm{CR}_0 - \mathrm{CR}_i}{\mathrm{CR}_0} \tag{3}$$

$$\mathrm{IE_W} = \frac{\mathrm{CR}_0 - \mathrm{CR}_i}{\mathrm{CR}_0} 100 \tag{4}$$

where ΔW is the average weight loss, S is the total surface area of the specimen and t is the immersion time. CR_0 and CR_i are corrosion rates in the absence and presence of various concentrations of PDDY, respectively. Corrosion rates and inhibitor efficiencies were evaluated and computed at different operating conditions.

Results and discussion

Mass loss measurements

Corrosion of mild steel in 1 M HCl in the absence and presence of various concentrations (5×10^{-6}, 10^{-5}, 5×10^{-5}, 10^{-4}, 5×10^{-4} and 10^{-3} M) of PDDY was studied by weight loss experiments at various temperatures (20, 30, 40, 50 and 60 °C). The corrosion rate (CR) in mg cm^{-2} h^{-1} and values of inhibition efficiency, obtained by 30 test runs of weight loss measurement after 3 hours of immersion in 1 M HCl solution, are summarized in Table 1. It was found that addition of PDDY inhibits corrosion of mild steel at all concentrations used in this study. As presented in Table 1, it is clear that corrosion rate increased with temperature and decreased with inhibitor concentration. Many similar results were obtained by other researchers, who already found that corrosion rate and inhibition efficiency depend on the concentration of the inhibitor and temperature of the medium [10,11].

Table 1. *Corrosion parameters obtained from weight loss measurements of mild steel after 3 h of immersion in 1 M HCl solution in the absence and presence of different concentrations of PDDY at various temperatures*

C / M	CR, mg cm^{-2} h^{-1}					IE$_W$, %				
	t / °C									
	20	30	40	50	60	20	30	40	50	60
blank	0.897	1.983	4.751	9.774	13.65	--	--	--	--	--
5×10^{-6}	0.361	0.807	2.419	6.271	9.510	59.755	59.304	49.084	35.840	30.330
1×10^{-5}	0.277	0.681	2.087	5.016	8.947	69.119	65.658	56.072	48.680	34.454
5×10^{-5}	0.194	0.552	1.649	4.354	8.161	78.372	72.163	65.291	55.453	40.212
1×10^{-4}	0.166	0.393	1.337	3.755	6.860	81.494	80.181	71.858	61.582	49.744
5×10^{-4}	0.074	0.336	0.925	2.598	4.944	91.750	83.056	80.530	73.419	63.780
1×10^{-3}	0.062	0.187	0.776	1.943	4.165	93.088	90.570	83.667	80.121	69.487

Inhibition efficiencies are for different concentrations of PPDY at different temperatures presented in Figure 2, where it is clearly seen that IE$_w$ reached the maximum value of 93.09 % for 10^{-3} M PPDY at 20 °C. It is well known that adsorption of inhibitor at steel surface is primarily responsible for the reduction of metal dissolution process in corrosive media [23]. The adsorption is enhanced by the presence of hetero atoms with lone pairs of electrons of the molecule inhibitors that facilitate the electrostatic adsorption on the steel surface by forming stable insoluble films. Data in Table 1 show that without inhibitor, the corrosion rate is as high as 0.897 (mg cm^{-2} h^{-1}), while in the presence of 10^{-3} M of inhibitor, CR value is reduced to 0.062 (mg cm^{-2} h^{-1}). From these measurements, we can conclude that PDDY is an effective inhibitor for mild steel in 1 M HCl solution.

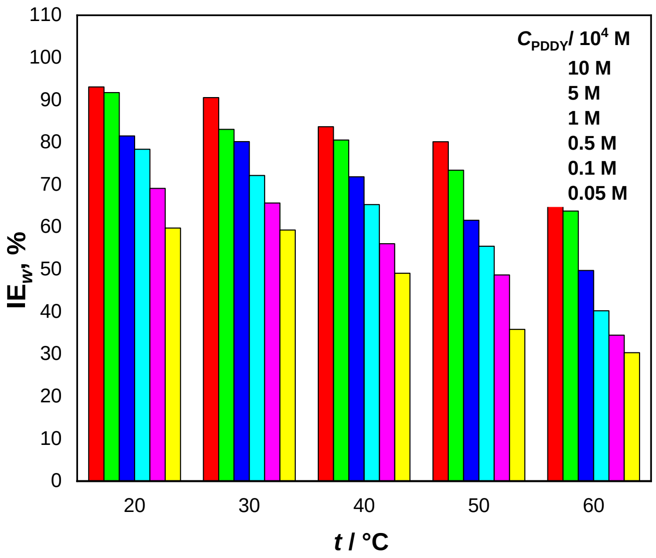

Figure 2. *Variation of inhibition efficiency with temperature after 3 hours of mild steel exposure in 1M HCl and various concentrations of PDDY*

Adsorption isotherm

Corrosion inhibition process is characterized by adsorption of the inhibitor on the metal surface. Adsorption of inhibitor is a displacement reaction in which the adsorbed water molecule is removed from the metal surface according to [13,14]:

$Org_{(sol)} + nH_2O_{(ads)} \leftrightarrow Org_{(ads)} + nH_2O_{(sol)}$

where n is the number of water molecules replaced by one organic molecule and $H_2O_{(ads)}$ is the water molecule on the metal surface. $Org_{(sol)}$ and $Org_{(ads)}$ are organic molecules in the aqueous solution and adsorbed on the metal surface, respectively.

For the effective adsorption of an inhibitor on the metal surface, the interaction force between metal and inhibitor must be greater than the interaction force of metal and water molecule [15]. Therefore, it is of great importance to find the appropriate adsorption isotherm that fits the experimental results. The experimental data have been tested with several adsorption isotherms including Langmuir, Temkin, Frumkin and Freundlich [16,17]. In this work, Langmuir adsorption isotherm was found as the best description of adsorption behavior of the studied compound. An expression of the Langmuir isotherm is given by [24,25]:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \qquad (5)$$

where C is inhibitor concentration, K_{ads} is equilibrium adsorption constant and θ is fractional surface coverage. According to eq. (5), the plot of (C/θ) versus C should yield straight line with nearly unit slope. Best results for Langmuir adsorption isotherm for PDDY on mild steel surface are presented in Figure 3. It is clear from Figure 3, however, that slopes of the straight lines are slightly greater than unity (*cf.* slope data referred in Figure 3). Therefore, it could be concluded that each PDDY unit occupies more than one adsorption site on the mild steel surface.

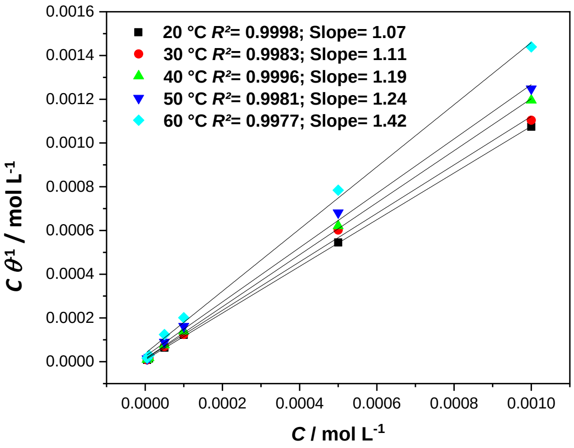

Figure 3. *Langmuir adsorption plots for mild steel in 1 M HCl containing different concentrations of PDDY at various temperatures*

To account for this phenomenon, a modified Langmuir adsorption isotherm could be applied, which is given by [7,19,20]:

$$\frac{C}{\theta} = \frac{n}{K_{\text{ads}}} + nC \qquad (6)$$

In eq. (6), n represents the slope of the respective line. The values of K_{ads} obtained from the values of slopes at different temperatures (Figure 3) were computed and gathered in the second column of Table 2. The increased values of K_{ads} for PDDY reflect the increasing adsorption capability due to structural formation on the metal surface [26,27]. K_{ads} is related to the standard Gibbs free energy of adsorption ($\Delta G^\circ_{\text{ads}}$) by the following equation

$$\Delta G_{\text{ads}}^0 = - RT \ln (55.5\, K_{\text{ads}}) \qquad (7)$$

where R is the universal gas constant (8.134 J K^{-1} mol^{-1}), T is temperature and 55.5 is molar concentration of water in the solution. The thermodynamic parameters derived from Langmuir isotherms are listed in Table 2. The values of ΔG°_{ads} for PDDY are all negative, what indicates the stability and spontaneity of adsorption of the inhibitor on the metal surface. The effectiveness of corrosion inhibition increases with increasing of negative ΔG°_{ads} values. Adsorption enthalpy and entropy ΔH°_{ads} and ΔS°_{ads} are determined graphically from the following equation

$$\Delta G^\circ_{ads} = \Delta H^\circ_{ads} - \Delta S^\circ_{ads} \tag{8}$$

Table 2. *Thermodynamic parameters of adsorption of PDDY on mild steel in 1 M HCl at various temperatures*

T / °C	K_{ads} / 10^{-4} L mol^{-1}	ΔG°_{ads} / kJ mol^{-1}	ΔH°_{ads} / kJ mol^{-1}	ΔS°_{ads} / kJ mol^{-1} K^{-1}
20	0.1374	-38.604	-24.36	0.049
30	8.935	-38.837		
40	9.580	-40.300		
50	5.424	-40.060		
60	3.968	-40.434		

It is well known that values of ΔG°_{ads} less negative than -20 kJ / mol are associated with the physical adsorption, characterized by an electrostatic interaction between the charged molecule and the charged metal. ΔG°_{ads} values around -40 kJ / mol or higher, are associated with the chemical adsorption where the sharing or transfer of organic molecules charge with the metal surface occurs [20-24]. The decrease observed for K_{ads} (Table 2), and also for IE_w (Figure 3) with increasing temperature, suggests that the PDDY molecules are physically adsorbed on the metal surface which favors their desorption processes. The value of ΔH°_{ads} provides further information about the mechanism of corrosion inhibition. The negative value of ΔH°_{ads} indicates that adsorption process is exothermic [3,7,23]. An exothermic adsorption process signifies chemical, physical or a mixture of both [24-27], whereas the endothermic process is attributed to chemisorption [28,29]. Results obtained from thermodynamic calculations for adsorption are in good agreement with the values of inhibition efficiency obtained from the weight loss.

Thermodynamic calculations for corrosion reaction

The stability of a corrosion inhibitor in an aggressive medium at some required operating temperature is very important for its practical applications. In this paper, the corrosion of mild steel in 1 M HCl was studied in the temperature range of 20-60 °C, in the absence and presence of different concentrations of PDDY, after 3 h of immersion time. Temperature dependence of corrosion rate (CR) is described by Arrhenius equation:

$$\mathrm{CR} = Ae^{-\frac{E_a}{RT}} \tag{9}$$

where A is the pre-exponential factor, E_a is activation energy for metal dissolution (corrosion) reaction, T is absolute temperature, and R is universal gas constant.

The dependence of logarithm of the corrosion rate (ln CR) on the reciprocal of the absolute temperature (1 / T) for mild steel in 1 M HCl is presented Figure 4. The corrosion rate of mild steel in acidic solution increases with rise of the temperature, regardless to the presence of inhibitor in the corrosive solution. In the case of uninhibited solution, the increase in corrosion rate was significant compared to inhibited cases involving a decrease in inhibition efficiency with increasing temperature up to 60 °C. The decrease in inhibition efficiency reveals that the film formed on the metal surface is less protective at higher temperatures, since the desorption rate of the inhibitor is greater at higher temperatures [30].

Thermodynamic parameters of the corrosion reaction, namely activation energy E_a, entropy (ΔS_a) and enthalpy (ΔH_a) were calculated using Arrhenius equation (9) and transition state theory equation [19]:

$$\mathrm{CR} = \frac{RT}{Nh} A\, \mathrm{e}^{\frac{\Delta S_a}{R}}\, e^{\frac{-\Delta H_a}{RT}} \tag{10}$$

In eq. (10), N is Avogadro's number (6.022×10^{23} mol^{-1}), and h is Planck's constant (6.63×10^{-34} J s). Eq. (10) is plotted in Figure 5 as ln (CR / T) against (1 / T).

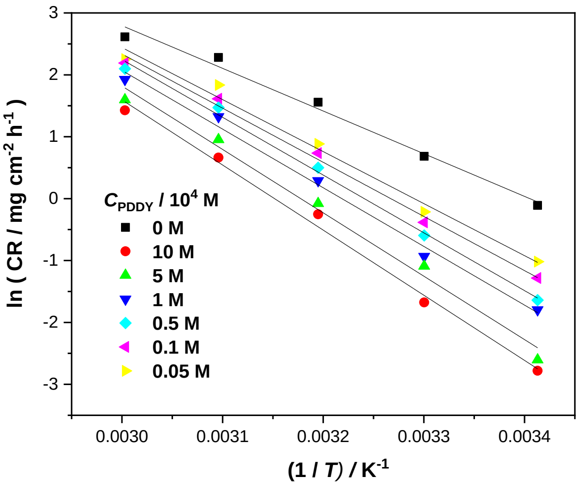

Figure 4. *Plots for mild steel corrosion rates in 1 M HCl in absence and presence of different concentrations of PDDY*

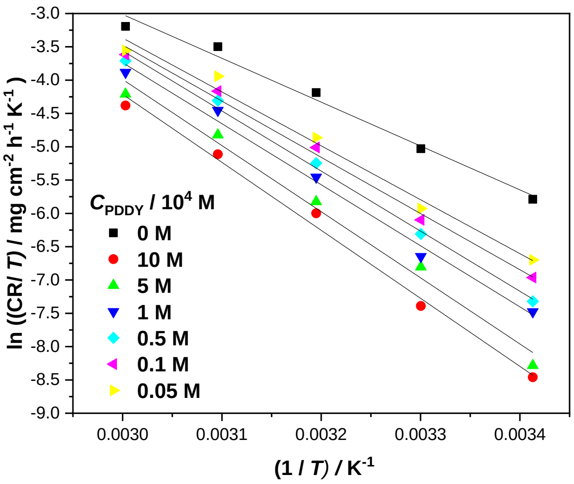

Figure 5. *Transition state plots for mild steel corrosion rates in 1 M HCl in absence and presence of different concentrations of PDDY*

The values of E_a and A, obtained from the slopes ($-E_a$ / R) and intercepts (ln A) of the lines in Figure 4, are displayed in Table 3, together with values of ΔH_a and ΔS_a deduced from the slopes ($-\Delta H_a$ / R) and intercepts [ln (R / Nh) +ΔS_a / R] of the lines in Figure 5.

Table 3. *Thermodynamic activation parameters of mild steel dissolution in 1 M HCl with and without various concentrations of PDDY*

C / 10^4 M	E_a / kJ mol^{-1}	ΔH_a / kJ mol^{-1}	ΔS_a / J mol^{-1} K^{-1}	ln A
blank	57.334	54.739	-58.37	23.483
0.05	69.877	67.283	-23.7	27.655
0.10	72.741	70.147	-16.0	28.584
0.50	77.604	75.009	-2.11	30.248
1.00	78.797	76.202	-0.0025	30.504
5.00	85.139	82.545	16.93	32.541
10.00	87.480	84.885	22.09	33.161

Examination of Table 3 shows that the activation energy values in the presence of PDDY ranged from 69.877 to 87.480 kJ mol^{-1}, revealing that the activation energy for metal dissolution increased in the presence of inhibitor. Also, E_a values in the presence of inhibitor are all higher than in absence of inhibitor, which indicates physical adsorption (electrostatic interaction). It has already been reported in the literature that inhibitors for which the activation energy in the inhibited solution is greater than that of the blank solution, $E_{a(inh)} > E_a$, are adsorbed on the substrate by electrostatic bonds (physisorption). At the other side, inhibitors where $E_{a(inh)} < E_a$, adsorb on the metal surface through strong bonds (chemisorption) [31,32]. The activation energy rises with increasing inhibitor concentration, suggesting strong adsorption of inhibitor molecules at the metal surface [33-37]. The values of ΔH_a and E_a are nearly the same and are higher in the presence of the inhibitor, indicating that the energy barrier of the corrosion reaction increased in the presence of inhibitor without changing the mechanism of dissolution [19]. The negative sign of the activation entropy values either in absence, or presence of the inhibitor may be explained by activated molecules in a higher order state than that at the initial stage [38,39]. At higher inhibitor concentrations (5×10^{-4} and 10^{-3} M), positive values of the entropy of activation ΔS_a were observed in the media. This indicates that the system passes from a more ordered state to a more random arrangement [40].

Morphological characterization

The scanning electron micrographs (SEM) of the mild steel surface in the absence and presence of 10^{-3} M of PDDY are presented in Figure 6. Comparison of Figures 6a and 6b shows that the surface of the sample is heavily damaged and severely corroded after 3 hours of immersion in 1 M HCl. Damages appear uniform with some lines resulting from polishing made before the testing. In the presence of PDDY, however, Figure 6c shows that the external morphology appears softer, indicating a protected surface. These images suggest that protection comes from the formation of PDDY layer on the mild steel surface that prevents the attack of acids.

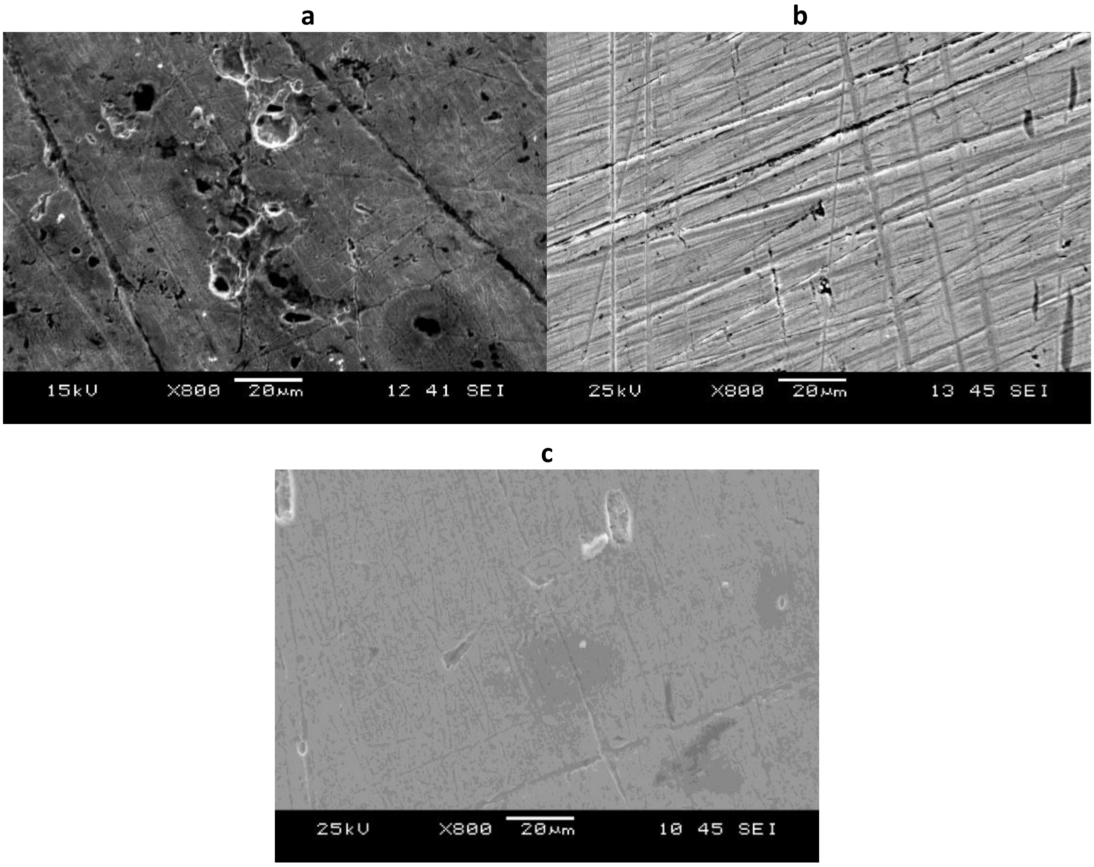

Figure 6. *SEM micrographs of mild steel surface: before corrosion (a); after immersion in 1 M HCl solution for 3 h at 20 °C (b); after immersion in 1 M HCl containing* 10^{-3} *M of PDDY for 3 h at 20 °C (c)*

Mathematical modeling

Mathematical regression analysis can be employed as a powerful tool for data representation [19]. The least squares method is the standard statistical approach in the regression analysis, used to find the optimum fit for a set of data points by minimizing the sum of the squares of the residuals of points from the plotted curve. In this study, two mathematical models were applied to illustrate the inhibition efficiency of PDDY for mild steel in 1.0 M HCl. The proposed mathematical models are classified into two groups, linear and quadratic models. Experimental data obtained in this work and presented above were used to construct the models that describe the relationship between the inhibition efficiency IE_W as a response, and temperature t and inhibitor concentration C as factors. Both models take into account the individual effect of each variable and the interaction between them.

Linear model

A linear mathematical model was used as a statistical tool aiming to predict the effect of the variables x_i and y_i which are respectively the temperature t and the inhibitor concentration to the function z_i which is the inhibitor efficiency IE_W. The proposed model is given by the equation (11):

$$z = a_1x + a_2y + a_3xy + a_4 + \varepsilon \tag{11}$$

where ε is the error term. The optimal model parameters a_i within the meaning of the least-squares method are these that minimize the quantity:

$$S(a_1, a_2, a_3, a_4) = \sum_{i=1}^{N} (a_1x + a_2y + a_3xy + a_4 + \varepsilon - z_i)^2 \tag{12}$$

In this expression, N is the number of experiments, a_i are constants representing the model parameters. The minimum of this expression is found when the partial derivatives ($\partial S/\partial a_i$) are equal to zero:

$$\frac{\partial S}{\partial a_i} = 0 \quad i = 1, 2, 3, 4 \tag{13}$$

This leads to a system of equations. Parameters of the model were estimated based on the least square method. The data were analyzed using computer program MATLAB that performs these calculations. Since $x = t$, $y = C$ and $z = IE_W$, the final model equation is:

$$IE_w = -0.865\, t + 17324.609\, C + 312.357\, TC + 92.125 \tag{14}$$

Based on the proposed linear model, the predicted values of inhibition efficiency as a function of temperature and inhibitor concentration are computed and listed in the first part of Table 4.

Quadratic model

The second proposed quadratic model equation was obtained by representing the inhibition efficiency IE_W by the response function z which can be expressed by the following equation:

$$z = a_1x^2 + a_2y^2 + a_3x + a_4y + a_5xy + a_6 + \varepsilon \tag{15}$$

where, ε is the error term, x the temperature, °C and y the inhibitor concentration (mol L^{-1}). Similarly, the optimal model parameters a_i within the meaning of the least-squares method are these which minimize the quantity:

$$S(a_1, a_2, a_3, a_4, a_5, a_6) = \sum_{i=1}^{N} (a_1x^2 + a_2y^2 + a_3x + a_4y + a_5xy + a_6 + \varepsilon - z_i)^2 \tag{16}$$

The minimum of this expression is found using the eq. (13). Using MATLAB software, parameters a_1-a_6 of the model were estimated and the final model equation is defined as:

$$IE_W = -0.01143\, t^2 - 5.19673\times10^7\, C^2 + 0.13615\, t + 80173.4333\, C + 0.01667\, TC + 69.6171 \qquad (17)$$

As for the linear model, the predicted values of inhibition efficiency were computed using the quadratic regression model and gathered in the second part of Table 4.

For analysis of the accuracy of the predicted results obtained with linear and quadratic regression models, we estimated the coefficient of determination known as R-squared (or R^2), using the equation below

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(z_i - z_{mi}\right)^2}{\sum_{i=1}^{N}\left(z_i - \bar{z}\right)^2} \qquad (18)$$

In this relationship z_i is experimental inhibition efficiency, z_{mi} predicted inhibition efficiency and $\bar{z}$ the average. The determination coefficient was found equal to 0.802 for the linear model and 0.902 for quadratic regression model, respectively.

In comparison with experimentally determined IE_W given in Table 1, data in Table 4 show similar IE_W values at all temperatures and concentrations of PDDY.

Figures 7 and 8 show the relationship between the values of the inhibitor efficiency obtained from the experimental work and those predicted by linear and quadratic regression models. It is obvious that almost 80 and 90 % of the data obtained from the linear and quadratic regression models are located on the line of equality, which means that the experimental and predicted values of inhibitory efficacy are close.

Table 4. *Inhibition efficiencies values computed by linear and quadratic regression models for different inhibitor concentrations and temperatures*

C / 10^4 M	IE_W, %									
	Linear regression					Quadratic regression				
	t / °C									
	20	30	40	50	60	20	30	40	50	60
0.05	74.944	66.310	57.676	49.042	40.408	68.168	63.814	57.185	48.249	37.038
0.01	75.062	66.443	57.825	49.207	40.588	68.565	64.211	57.572	48.646	37.435
0.50	76.005	67.511	59.018	50.524	42.031	71.647	67.293	60.654	51.728	40.517
1.00	77.183	68.846	60.509	52.171	43.834	75.266	70.912	64.273	55.347	44.136
5.00	86.612	79.524	72.436	65.348	58.261	94.863	90.510	83.870	74.945	63.734
10.00	98.398	92.872	87.346	81.820	76.294	95.975	91.621	84.982	76.057	64.845

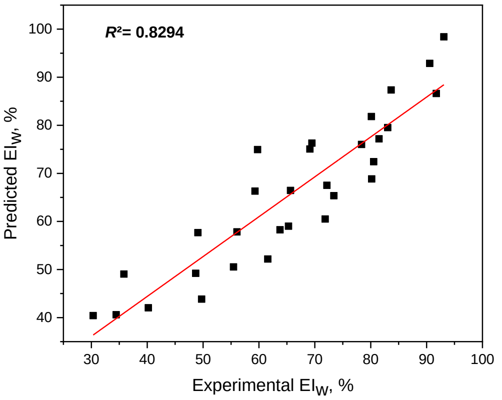

Figure 7. *Fitting curves of predicted against experimental inhibition efficiency obtained by the linear regression model*

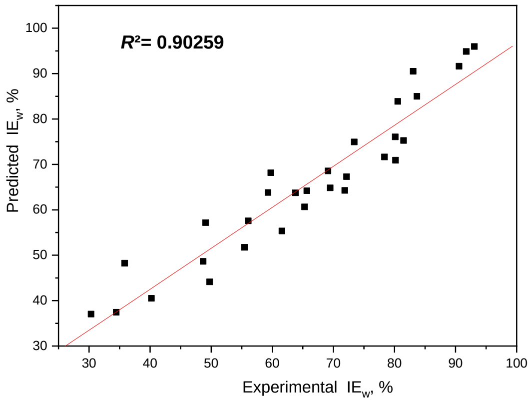

Figure 8. *Fitting curves of predicted against experimental inhibition efficiency obtained by the quadratic regression model*

This is quite true because the determination coefficients were R^2= 0.829 for linear model and R^2 = 0.920 for quadratic regression model. According to [19], when R^2 is < 0.30 the relationship is weak, for R^2 = 0.50 and 0.70, the relationship is important, while for R^2 > 0.90, the relationship is powerful. Based on correlation coefficients, the present results indicate a strong relationship between experimental and mathematical data, indicating the concordance between the experimental and the predicted results.

As shown in Figure 9, examination of data provided by linear and quadratic regression models and presented as surface plots, reveals that the addition of PDDY at different concentrations decreases the corrosion rate of mild steel. The inhibition efficiency increases with increasing inhibitor concentration (red zone) and decreases with increasing temperature (blue zone). This can be explained by a regression of adsorption induced by temperature rise. At concentration 10^{-3} M and temperature 20 °C, PDDY exhibits maximum inhibition efficiency for both models: 98.398 % (linear model) and 95.975 % (quadratic regression). A comparison with the experimentally found value of inhibition efficiency of 93.088 % shows more reliability of the quadratic regression model than the linear model.

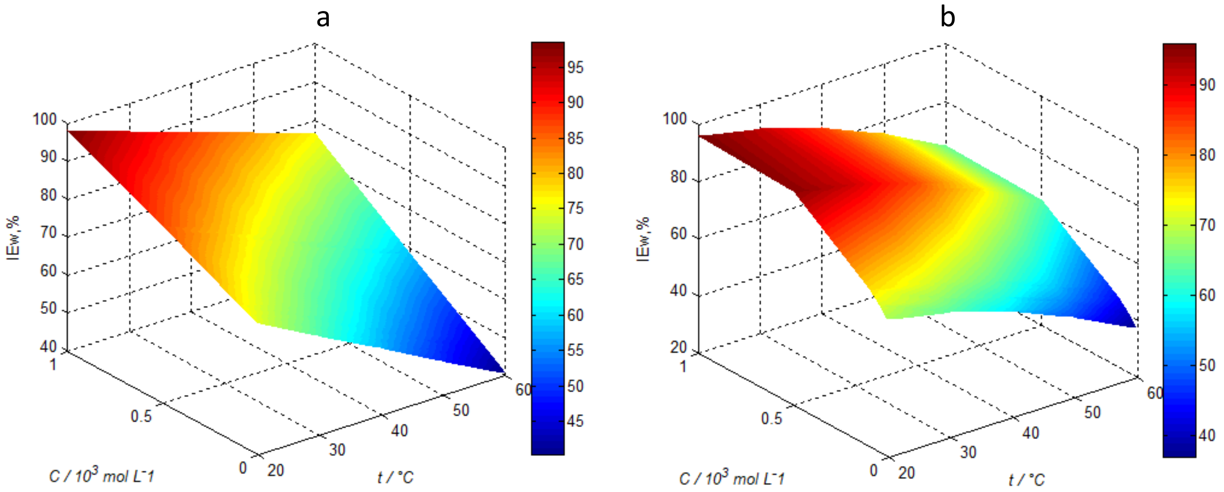

Figure 9. *Surface plot for inhibition efficiency, temperature and inhibitor concentration based on: a) linear regression model; b) quadratic regression model*

Conclusion

In this paper, the inhibition effect and adsorption behavior of the organic compound 3-(1,3-dithian-2-ylidene) pentane-2,4 dione (PDDY) on mild steel in 1 M HCl medium were examined, using the weight loss method, morphological characterization and mathematical modeling. The following conclusions are drawn:

- The inhibition efficiency of PDDY increases with increasing inhibitor concentration in the range of 5×10^{-6} to 10^{-3} M, and reaches the maximum value of 93.088 % in the presence of 10^{-3} M of PDDY. The thermodynamic study showed that adsorption of this inhibitor on the mild steel surface is spontaneous and follows the Langmuir adsorption isotherm model. The negative value of the Gibbs free energy of adsorption (ΔG_{ads}) is indicative for a strong interaction between inhibitor molecules and the surface of mild steel.
- The evolution of the corrosion rate of mild steel in the corrosive solution alone (1 M HCl) shows a regular and rapid growth, confirming an increasing metallic dissolution with increasing temperature. The inhibitory efficiency of PDDY decreases, while corrosion rate increases with temperature in the range 20 to 60 °C for all inhibitor concentrations used. This behavior illustrates physisorption of PDDY molecules on mild steel surface.

- Formation of a protective layer on mild steel surface by the inhibitor observed by SEM, confirmed high performance of the inhibitive effect of PDDY.
- Linear and quadratic mathematical regression models are found suitable to represent the experimental data with high correlation coefficients. Experimentally determined inhibition efficiency of 93.088 % is found closer to the result predicted by the quadratic regression model. The predicted result also confirm that inhibition efficiency is influenced by temperature, inhibitor concentration and their combined effect.

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