Corrosion Inhibition Performance of Two Ketene Dithioacetal Derivatives for Stainless Steel in Hydrochloric Acid Solution

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ABSTRACT

The methyl 2-(1,3-dithietan-2-ylidene)-3-oxobutanoate (MDYO) and 2-(1,3-dithietan-2-ylidene) cyclohexane-1,3-dione (DYCD) were synthesized and tested at various concentrations as corrosion inhibitors for 316L stainless steel in 1 M HCl using weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), surface analysis techniques (SEM / EDX and Raman spectroscopy) and Functional Density Theory (DFT) was also used to calculate quantum parameters. The obtained results indicated that the inhibition efficiency of MDYO and DYCD increases with their concentration, and the highest value of corrosion inhibition efficiency was determined in the range of concentrations investigated (0.01×10^{-3} - 10^{-3} M). Polarization curves (Tafel extrapolation) showed that both compounds act as mixed-type inhibitors in 1M HCl solutions. Electrochemical impedance spectra (Nyquist plots) are characterized by a capacitive loop observed at high frequencies, and another small inductive loop near low frequencies. The thermodynamic data of adsorption of the two compounds on the stainless steel surface and the activation energies were determined and then discussed. Analysis of experimental results shows that MDYO and DYCD inhibitors adsorb to the metal surface according to the Langmuir model and the mechanism of adsorption of both inhibitors involves physisorption. SEM-EDX results confirm the existence of an inhibitor protective film on the stainless steel surface. The results derived from theoretical calculations supported the experimental observation.

Keywords : Corrosion Inhibition, Ketene Dithioacetal Derivatives, Stainless Steel, Hydrochloric Acid

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1. Introduction

Steel is used in all aspects of our life, and it's the most significant engineering and construction material in the world [1]. There are several known published grades of steel. The corrosion resistance on stainless steels is fundamentally based on the presence of alloying elements in solid solution, mainly chromium, nickel, and molybdenum. Stainless steel has a vast passivity range, extending at room temperature from pH below 2 to concentrate alkaline media; however, most stainless steel cannot tolerate aggressive HCl solutions. Indeed, acid solutions are

widely used in various industrial processes, and hydrochloric acid is most commonly used due to its low cost and effective cleaning action than other mineral acids [2,3].

Organic molecules are protective barriers between aggressive environments and metal or their alloys. Several works conducted in this field show that most of these compounds act by adsorption on the metal surface, and that the mode of action depends among other things on the nature, the surface state, and the surface charge of the metal, the type of the aggressive electrolyte, the physico-chemical properties of the inhibitor and the chemical structure of the inhibitors [4]. This adsorption produces a uniform film that protects the metal surface against the aggressive medium, thus reducing the corrosion attack, leading to the metal's dissolution [5]. The literature shows that compounds containing unsaturated bonds and/or polar atoms, such as oxygen (O), nitrogen (N), and

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Table 1. Molecular structure of inhibitors.

Inhibitor	Structure
Methyl 2-(1, 3-dithietan-2-ylidene)-3-oxobutanoate (MDYO)	
2-(1, 3-dithietan-2-ylidene)cyclohexane-1,3-dione (DYCD)	

sulfur (S), are suitable inhibitors for metal corrosion, and in particular, steel in acidic environments [6-8]. It also appears from the literature that the inhibitory capacities of many organic molecules have been studied and confirmed in the case of corrosion of stainless steel in hydrochloric acid [9,10]. Schiff base (S_2N_2 -Schiff base) [11], bis-N,S-bidentate Schiffbase [12], and recently azole compounds [13] have shown promising results, and their inhibitory efficiency could be linked to the presence of heteroatoms in their molecular structure. These results have led us to use some ketene dithioacetal derivatives as organic metal corrosion inhibitors in acidic environments [14,15]. The present work is an extension of our precedents investigations, and it concerns the synthesis and characterization of two ketene dithioacetal derivatives, namely methyl 2-(1,3-dithietan-2-ylidene)-3-oxobutanoate (MDYO) and 2-(1,3-dithietan-2-ylidene)cyclohexane-1,3-dione (DYCD) (Table 1). The choice of these compounds was based upon environmental, economic, and molecular structure regard. Indeed, these derivatives have low toxicity and good solubility in hydrochloric acid solutions.

Moreover, these molecules are easily prepared in high yield and purity using non expensive chemical materials with multiple reactive sites (S, O, and π -

electrons) that should facilitate their adsorption and improve their efficiency to be used as corrosion inhibitors. The corrosion inhibition efficiency of the two prepared compounds on 316 L steel in a 1 M HCl solution was examined. The study was carried out by weight loss, electrochemical impedance spectroscopy, polarization curves, Raman spectroscopy, and scanning electron microscopy. Finally, functional density theory (FDT) was also used to corroborate the experimental results.

2. Experimental

2.1. Materials

The material used as the working electrode in this study is 316L stainless steel, the composition of which is (%): 0.03 C, 17.2 Cr, 10.58 Ni, 2.31 Mo, 0.67 Si, 0.19 Mn, 0.04 P, 0.02 S, 0.09 N, and Fe presents the balance. The stainless steel samples (disc 1.2 cm in diameter and 0.3 cm thick) were mechanically polished with abrasive papers ranging from 400, 800, 1200, and 2000 and then degreased with acetone and finally rinsed with distilled water before being dried at room temperature and weighed. The prepared 316 L stainless steel was used in gravimetric and electrochemical measurements. The electrolyte solution is a 1 M hydrochloric acid solution that is prepared using a commercial 37% hydrochloric acid solution (VWR PROLAB) and distilled water.

2.2. Synthesis of inhibitors

The two studied compounds (MDYO and DYCD) listed in Table 1 were synthesized according to the reported procedure [15]. Scheme 1 represents the method of synthesis.

The methyl 2-(1,3-dithietan-2-ylidene)-3-oxobutanoate (MDYO) was synthesized as follows: K_2CO_3 (42 g, 0.3 mol) and methyl acetoacetate (0.1 mol) in 50 mL of DMF were agitated magnetically. Carbon

Scheme 1. The general method of the synthesis reaction of inhibitors.

disulfide (9 mL, 0.15 mol) was added, and the agitation was maintained for 10 min before adding Diiodomethane (0.12 mol), drop by drop for 20 min. After 7 hours of agitation at room temperature, ice water (500 mL) was added to the reaction mixture. The precipitate formed was filtered, dried, and recrystallized in ethanol.

The 2-(1,3-dithietan-2-ylidene)cyclohexane-1,3-dione (DYCD) was synthesized by a similar procedure (MDYO) using 1,3 cyclohexanedione instead of methyl acetoacetate. White crystals were obtained for both products prepared. The structure characterization of the prepared compounds was carried out using ^1H NMR, ^{13}C NMR, IR, UV-vis, and melting point. The studied inhibitors were used at different concentrations ranging from 1 to 0.01 mM. Spectroscopic and physical data are summarized below:

Methyl 2-(1,3-dithietan-2-ylidene)-3-oxobutanoate[16] (**MDYO**): Yield 86%; m.p. 118°C; UV (H_2O) λ_{max} , 320 nm (ϵ 14050); IR (KBr) cm^{-1} : 1687(C=O, CO_2Me), 1618 (C=O, COMe), 1085-1225 (C-O); ^1H NMR (CDCl_3) δ_{ppm} : 4.03 (s, 2H, CH_2), 3.72 (s, 3H, $\text{CH}_3\text{-O-CO}$), 2.35 (s, 3H, $\text{CH}_3\text{-CO}$); ^{13}C NMR (CDCl_3) δ_{ppm} : 196.55 ($\text{CH}_3\text{-C=O}$), 188.50 (C=C-S), 165.60 ($\text{CH}_3\text{-O-CO}$), 113.69 (C=C-S), 51.24 ($\text{CH}_3\text{-O-CO}$), 30.11 ($\text{CH}_3\text{-CO}$), 28.9 (C $_2$).

2-(1,3-dithietan-2-ylidene)cyclohexane-1,3-dione (**DYCD**): Yield 81%; m.p. 214°C; UV (H_2O) λ_{max} , 335 nm (ϵ 18760); IR (KBr) cm^{-1} : 1640 (C=O), ^1H NMR (CDCl_3) δ_{ppm} : 4.35 (s, 2H, C $_2$ -S), 2.52 (t, $J=6.5\text{Hz}$, 4H, C $_2$ -CH $_2$ -CH $_2$), 1.97 (q, $J=6.5\text{Hz}$, 2H, CH $_2$ -C $_2$ -CH $_2$); ^{13}C NMR (CDCl_3) δ_{ppm} : 197.28 (C=O), 189.73 (C=C-S), 119.93 (C=C-S), 37.31 (CH $_2$ -C $_2$ -CH $_2$), 33.39 (C $_2$ -S), 18.62 (CH $_2$ -C $_2$ -CH $_2$).

2.3. Weight loss measurements

For weight loss measurements, the samples were weighed and immersed in a volume of 100 mL in the vertical position in the absence and, in the presence of different concentrations of inhibitors (1, 0.5, 0.1, 0.05, and $0.01 \times 10^{-3} \text{ mol L}^{-1}$) at different temperatures (25-65°C) with immersion time of 1 to 24 hours. The exposed stainless steel surface is 2.26 cm^2 . After immersion, the samples were removed, washed with distilled water, dried, and then weighed using an analytical balance (OHAUS AR124CN). Weight loss is the average of three tests carried out under the same conditions for each concentration.

Fig. 1. Langmuir adsorption isotherms obtained for 316L stainless steel in 1 M HCl in the presence of MDYO and DYCD at 298 K.

2.4. Electrochemical measurements

All the electrochemical tests were realized with a three-electrode arrangement. The working electrode is made from stainless steel 316 L with a surface exposed area of 0.636 cm^2 . The counter electrode was a platinum electrode, whereas the reference electrode was a saturated calomel electrode (ECS). The PGP 201 Radiometer Potentiostat-Galvanostat, controlled by the VoltaMaster 1 software, was used to obtain the polarization curves. After 60 min of immersion, the scanning of potentials was carried out between: -700 mV/SCE to -200 mV/SCE with a scanning speed of 20 mV/min. The electrochemical impedance diagrams were performed over a frequency range of 100 kHz - 10 mHz and an amplitude of 10 mV at the corrosion potential after 60 min of immersion using a Bio-Logic SP 300 Potentiostat-Galvanostat controlled by the EC-Lab V10.40 software.

2.5. Surface analysis

The study of the surface morphology of steel in the absence and, in the presence of inhibitor in 1 M HCl was carried out using a Hitachi S-4800 SEM-EDX scanning electron microscope with an accelerating voltage of 20 kV after 3 hours of immersion.

2.6. Raman spectroscopy

The Raman spectra were obtained using a Raman spectroscope (Horiba Scientific) in 50-2000 cm^{-2} intervals at a power of 17 mW and a wavelength of 633 nm, after 24 hours of immersion.

2.7. Theoretical calculation

The investigated compounds were, at first, initially arranged and minimized using the Avogadro program [17], applying the MMFF94 force field. The quantum chemical calculations of DFT were performed with the ORCA 4.0.1.2 computer package, under an open-source code developed by Prof. Frank Neese [18,19]. The optimization of the geometry of the studied compounds (Table 1) was performed using the functional CAM-B3LYP [20] and employing sets of triple- ζ quality bases def2-TZVPP [21]. Finally, the natural population analysis (NPA) was performed with the JANPA program (version 1.04) [22].

To evaluate our experimental results, we calculated the global reactivity descriptors, such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE_{Gap}), ionization potential (I), electron affinity (A), molecular volume for van der Waals (V^{vdw}), surface area (SA), dipolar moment (μ), polarizability $\langle\alpha\rangle$, electronegativity (χ), chemical potential (π), global hardness (η), global smoothness (σ) and electrophilicity (ω).

$$I = -E_{HOMO} \quad (1)$$

$$A = -E_{LUMO} \quad (2)$$

$$\Delta E_{Gap} = E_{LUMO} - E_{HOMO} \quad (3)$$

$$\chi = -\pi = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (4)$$

$$\eta = -\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \quad (5)$$

$$\chi = \frac{I + A}{2} \quad (6)$$

$$\eta = \frac{I - A}{2} \quad (7)$$

$$\sigma = \frac{1}{\eta} = \frac{2}{I - A} \quad (8)$$

$$\Delta N = \frac{\chi_M - \chi_{inh}}{2(\eta_M + \eta_{inh})} \quad (9)$$

where χ_M and χ_{inh} are absolute electronegativity values of metal and inhibitor, and η_M and η_{inh} are abso-

lute hardness values of metal and inhibitor, respectively. When the metal is iron ($M = Fe$), $\chi_{Fe} = 7$ eV, $\eta_{Fe} = 0$ eV [23], this equation can be rewritten as follows:

$$\Delta N = \frac{7 - \chi_{inh}}{2\eta_{inh}} \quad (10)$$

3. Results and Discussion

3.1. Weight loss measurements

3.1.1. Effect of concentration

The corrosion rate W_{corr} and inhibition efficiency $IE_W\%$ were calculated using equation 11 and 12. The degree of surface coverage (θ) for different concentrations of the inhibitor in acidic media was evaluated by weight loss measurements using equation 13 [24]. The values of the corrosion rate W_{corr} , the inhibition efficiency $IE_W\%$ and degree of surface coverage (θ) obtained are summarized in Table 2.

$$W_{corr} = \frac{\Delta m}{St} \quad (11)$$

where Δm is the weight loss (mg), S is the stainless steel sample surface (cm^2), t is the immersion time (s).

$$IE_W\% = \left[\frac{W_{corr}^0 - W_{corr}}{W_{corr}^0} \right] \times 100 \quad (12)$$

$$\theta = \left[\frac{W_{corr}^0 - W_{corr}}{W_{corr}^0} \right] \quad (13)$$

where W_{corr}^0 and W_{corr} are the corrosion rate in the absence, and presence of tested inhibitors, respectively.

From Table 2, we found that increasing the concentration of the inhibitor leads to a decrease in the corrosion rate and an increase in the coverage surface. Therefore the inhibitory performance of the inhibitor increases as well. We can explain this phenomenon by increasing the concentrations of both inhibitors leads to increasing the surface area of the steel covered by the adsorbed molecules. As a result, the majority of the active corrosion sites are blocked, resulting in higher inhibition efficiency [25,26]. The inhibi-

Table 2. The corrosion rate values, W_{corr} inhibitory efficiency, $IE_w\%$ and surface coverage, θ in the absence and presence of tested inhibitors.

Inhibitors	C (mM)	W_{corr} (mg cm ⁻² h ⁻¹)	θ	IE_w (%)
MDYO	Blanc	0.266	-	-
	1.00	0.030	0.887	88.72
	0.50	0.044	0.835	83.46
	0.10	0.089	0.669	66.92
	0.05	0.118	0.556	55.64
	0.01	0.133	0.500	50.00
DYCD	1.00	0.044	0.835	83.46
	0.50	0.059	0.779	77.82
	0.10	0.103	0.613	61.28
	0.05	0.118	0.556	55.64
	0.01	0.147	0.447	44.74

tory efficacy reaches a maximum value of 88.72% for MDYO and 83.46% for DYCD at a concentration of 10⁻³ M (Table 2). The inhibitory efficiency increased in the following order: MDYO > DYCD. This difference in efficiency can be explained by the effect of the nature and number of the electron donor group in each compound. The presence of the methoxy group (-OCH₃) in the structure of MDYO probably marks the difference and favors the adsorption of the molecules on the surface of stainless steel.

3.1.2. Adsorption isotherm

The corrosion inhibition of metal by organic compounds is explained by the adsorption of the organic molecules on the metal surface. Adsorption isotherms are, indeed, an important complement likely to determine the electrochemical mechanism that leads to the adsorption of these organic compounds on the surface. To describe the adsorption behavior of the studied inhibitors, several adsorption isotherms were tested: Langmuir, Temkin, and Frumkin. These isotherms are characterized by the following relationships [27,28]:

$$\text{Langmuir } \frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (14)$$

$$\text{Frumkin } \left(\frac{\theta}{1-\theta} \right) \exp(2a\theta) = K_{\text{ads}} C_{\text{inh}} \quad (15)$$

$$\text{Temkin } \exp(-2a\theta) = K_{\text{ads}} C_{\text{inh}} \quad (16)$$

where θ denotes the degree of surface coverage, K_{ads} is the adsorption coefficient (or the equilibrium constant of the adsorption process), C_{inh} is the concentration of the inhibitor in the solution, and a is an interaction constant between adsorbed particles.

The degree of surface coverage (θ) obtained by the weight loss method was plotted as a function of inhibitor concentration to evaluate the best isotherm that fits the data obtained in the present study. The correlation coefficient (R^2) was used to select the appropriate isotherm. From Table 3, we can see that the linear correlation coefficient is close to 1, and also the value of the slope is close to 1 only for the Langmuir isotherm, which shows that the adsorption of MDYO and DYCD on the surface of the steel in hydrochloric acid obeys the Langmuir isotherm. The values of K_{ads} have also been calculated (Table 4).

The adsorption constant K_{ads} is linked to the standard free energy of adsorption (ΔG_{ads}^0) by the following equation:

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5 K_{\text{ads}}) \quad (17)$$

where R is the universal gas constant, T is the temperature and 55.5 is the molar concentration of water in the solution (mol L⁻¹).

Table 4 summarizes the values of K_{ads} determined from the ordinate intersection of the Langmuir lines, and the standard free energy of adsorption, ΔG_{ads}^0 calculated for the two inhibitors. The negative sign of

Table 3. Parameters of different curves of the Langmuir, Frumkin, and Temkin adsorption isotherms of the MDYO and DYCD at 298 K

Isotherms	Curves	Parameters	
		MDYO	DYCD
Langmuir	$\frac{C_{inh}}{\theta} = f(C_{inh})$	$R^2 = 0.99949$ Slop = 1.10593	$R^2 = 0.99935$ Slop = 1.17784
Frumkin	$\ln \left[\frac{C_{inh}(1-\theta)}{\theta} \right] = f(\theta)$	$R^2 = 0.91889$ Slop = 5.41492	$R^2 = 0.98172$ Slop = 6.75719
Temkin	$\theta = f(\ln C_{inh})$	$R^2 = 0.98009$ Slop = 0.09017	$R^2 = 0.99578$ Slop = 0.08651

Table 4. Thermodynamic parameters of adsorption of MDYO and DY CD in 1M HCl.

Inhibitors	K_{ads} (mM ⁻¹)	ΔG_{ads}^o (kJ mol ⁻¹)
MDYO	33.30	-18.64
DYCD	31.10	-18.47

the calculated values of ΔG_{ads}^o (Table 4) reveals the stability of the adsorbed layer and the spontaneity of the adsorption process [7,29]. Generally when the value of ΔG_{ads}^o is close to/or more negative than -40 KJ mol⁻¹, this corresponds to a charge transfer between the molecules of the inhibitor and the metal surface with the formation of covalent bonds (chemisorption). In contrast, the values of ΔG_{ads}^o close to/or less negative than 20 KJ mol⁻¹ are related to electrostatic interactions of the physical adsorption of the inhibitor on the metal surface (physisorption). In our case, the obtained values were close to -20 KJ mol⁻¹ (-18.47 KJ mol⁻¹ for DYCD and -18.64 KJ mol⁻¹ for MDYO) which shows that the mechanism of adsorption of the molecules of the two inhibitors on the surface of the stainless steel in 1 M HCl involves physisorption [30,31]. The higher value of ΔG_{ads}^o in the case of MDYO indicates that MDYO is more adsorbed than DYCD on the metal surface. This result is in good agreement with the results obtained from weight loss.

3.1.3. Effect of solution temperature

Temperature has an important effect on the action of inhibitors. The Arrhenius equation gives the activation energy (E_a) and represents the reliance of the corrosion rate on temperature (Eq. 18) [30].

$$W = A \exp\left(\frac{-E_a}{RT}\right) \quad (18)$$

where T is the temperature, A is the pre-exponential factor of Arrhenius and R is the constant of the ideal gases. The alternative formula of the Arrhenius equation (Eq.19) is used to calculate the entropy, ΔS_a^o , and the enthalpy ΔH_a^o of activation.

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^o}{R}\right) \exp\left(-\frac{\Delta H_a^o}{RT}\right) \quad (19)$$

with: N is the Avogadro number and h is Planck's constant.

Fig. 2 shows the variation of the corrosion rate logarithm as a function of the absolute temperature inverse. This variation in $\ln W = f(1/T)$ is a straight line for both compounds without and with different concentrations of inhibitors. The activation energy values without and with inhibitors MDYO and DYCD are given in Table 5. We note that an increase in the activation energies for MDYO and DYCD compared to a blank (1 M HCl). The change of activation energy can be attributed to the physical (electrostatic) adsorption of these inhibitors on the stainless steel surface, which occurred during the first step [32]. Furthermore, the increase in E_a can be correlated with the increase in the thickness of the double layer [33]. However, the adsorption process could not be simplified and classified as a chemical or physical process.

Due to the competitive adsorption of the inhibitor molecules with that of H₂O, the type of adsorption

Table 5. The values of activation parameters (E_a , ΔH_a° , and ΔS_a°) for the corrosion of 316 L SS in 1 M HCl without and with 1 mM of MDYO or DYCD.

Inhibitors	E_a (kJ mol ⁻¹)	ΔH_a° (kJ mol ⁻¹)	ΔS_a° (J mol ⁻¹ K ⁻¹)
Blanc	14.54	11.90	-216.16
MDYO	58.04	55.40	-87.52
DYCD	47.91	45.28	-118.71

Fig. 2. Arrhenius plots of 316L SS in 1 M HCl solution without and with 10^{-3} M of MDYO and DYCD.

Fig. 3. Transition Arrhenius plots of 316L SS in 1 M HCl solution without and with 10^{-3} M of MDYO and DYCD.

criteria acquired from the change in activation energy cannot be considered stable. Therefore, the adsorption of MDYO and DYCD on the stainless steel surface from the HCl solution occurred through chemical and physical transactions largely synchronized with the first step [34]. Schmidt and Huang [35] have found that organic molecules stop partial anodic and cathodic reactions on the metal surface, and a parallel

reaction takes place on the covered part, but this reaction is less important than the reaction on the exposed part of the metal surface. We noted that the value of E_a obtained for MDYO was higher than that obtained for DYCD confirming the better inhibitory efficacy of MDYO.

The activation parameters can be determined from the variation of $\ln (W/T)$ as a function of the inverse temperature, where the slope of the obtained line is $(-\Delta H_a^\circ / RT)$, and the intercept is $(\ln R/Nh + \Delta S_a^\circ / R)$. The values of the enthalpies, ΔH_a° , and the entropies, ΔS_a° , are given in Table 5. The high positive values of ΔH_a° reveal the endothermic nature of the stainless steel dissolution process [36]. In the presence of MDYO and DYCD, the lower negative values of the entropy, ΔS_a° , indicate that the complex activated in the determining step of the rate represents an association rather than a dissociation, meaning that there was a decrease disorder when transforming reagents into an activated complex [37,38]. This phenomenon has been attributed by Zhou [39] to the adsorption of inhibitor molecules on the metal surface during the desorption of water molecules (H_2O).

3.2. Potentiodynamic polarization results

The electrochemical behaviour of the stainless steel sample in inhibited and uninhibited solutions is shown in Fig. 4. The electrochemical parameters obtained from the polarization curves, including corrosion potential (E_{corr}), corrosion current densities (I_{corr}), Tafel cathodic slopes (β_c), and inhibition efficiencies ($IEp\%$), are summarized in Table 6.

The cathodic polarization curves represent the evolution of hydrogen, while the anodic polarization curves represent the dissolution of stainless steel. The cathodic curves of the studied inhibitors showed the same trend, and cathodic Tafel slopes were approximately the same. This result indicated the H^+ ion reduction cathodic reaction's slowing down with no change in the reaction mechanism [40]. Further-

more, the cathodic curves showed that the cathodic process was not controlled by diffusion. These curves present linear parts (Tafel line), which confirm that

the hydrogen reduction reaction is accomplished at the stainless steel surface according to a pure activation mechanism.

Furthermore, a slight modification in Tafel cathodic slopes β_c with increasing inhibitors concentrations was observed for both inhibitors, which confirm that the evolutions of hydrogen were similar at the different concentrations of MDYO and DYCD in 1M HCl (Table 6), and it takes place according to a pure activation mechanism. We also noted that the presence of both MDYO and DYCD inhibitors in 1M HCl shifts the corrosion potential to more noble (electropositive) values for the different concentrations; this was due to the interactions of Cl^- ions with MDYO and DYCD. This shift was less than -80 mV compared to the value obtained without the inhibitor, which confirms the mixed character of the two inhibitors [41,42].

From Fig. 4, it is clear that anodic branches of curves present a deviation from Tafel's behaviour. This deviation is related to the deposition of corrosion products on the surface of stainless steel [43]. Also, it have been noted that anodic polarization may sometimes produce concentration effects, due to passivation and dissolution, as well as roughening of the surface, which can lead to deviation from Tafel behavior. The extrapolation of the cathode branch would be sufficient to calculate the corrosion current by extrapolating Tafel to the corrosion potential [44,45]. Also, extrapolation of the Tafel cathodic region to a zero overvoltage would give the net rate of the cathodic reaction to the corrosion potential. It is also the net rate of anodic reaction to corrosion

Fig. 4. Tafel polarization curves for corrosion of 316L stainless steel in 1 M HCl in the absence, and presence of various concentrations of inhibitors: (a) MDYO and (b) DYCD, $v = 1 \text{ mV s}^{-1}$ and at room temperature.

Table 6. Electrochemical parameters and inhibitory efficiency for different concentrations of MDYO and DYCD for corrosion of 316L steel in 1 M HCl obtained by plotting the polarization curves.

Inhibitors	C (mM)	$-E_{\text{corr}}$ (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} ($\mu\text{A cm}^{-2}$)	IEp (%)
MDYO	Blank	420.00	126.7	467.74	-
	1.00	368.57	106.67	20.89	95.53
	0.50	374.29	105.88	39.81	91.49
	0.10	405.00	102.56	120.23	74.30
	0.05	407.50	122.64	204.17	56.35
	0.01	410.00	102.56	237.14	49.30
DYCD	1.00	345.00	138.69	23.71	94.93
	0.50	358.33	129.63	44.67	90.45
	0.10	380.00	101.29	56.23	82.34
	0.05	396.67	106.87	100.00	66.12
	0.01	400.00	106.38	151.36	61.98

potential that has been verified by other non-electrochemical techniques [46].

In our case, due to the phenomenon of passivation on the anodic branch in potentiodynamic polarization curves, the anodic Tafel curves present a very short linear behaviour, so it was difficult to determine the corresponding slope of Tafel in this branch [47,48]. Tafel linear segments of the cathodic part were extrapolated to the corrosion potential to obtain corrosion current densities (I_{corr}). From Table 6, the corrosion current density has decreased significantly for all the concentrations compared to that obtained without inhibitors, especially for the 10^{-3} M concentration.

The $IE_p\%$ inhibition efficiency was evaluated from the I_{corr} values measured using the relationship [49]:

$$IE_p = \frac{i_{\text{corr}}^a - i_{\text{corr}}^{\text{inh}}}{i_{\text{corr}}^a} \times 100 \quad (20)$$

where, i_{corr}^a and $i_{\text{corr}}^{\text{inh}}$ are the corrosion current densities in the absence, and presence of inhibitor, respectively. The inhibition efficiency values, Table 6, showed that MDYO and DYCD acted as a very effective corrosion inhibitor for stainless steel in a 1 mol L⁻¹ HCl solution and that their inhibition capabilities increased with increasing concentrations. A maximum inhibition efficiency, 95.53%, was obtained for MDYO and 94.93% for DYCD at a concentration of 10^{-3} M. These results are consistent with the results obtained by weight loss measurements (MDYO > DYCD).

3.3. Electrochemical impedance spectroscopy results

The measurement of the electrochemical impedance makes it possible to differentiate the reaction phenomena of an electrochemical system by their relaxation time. Only fast processes are characterized at high frequencies; as the applied frequency decreases, the contribution of slower steps, such as transport or diffusion phenomena in solution, will appear [50]. For this purpose, electrochemical impedance measurements were carried out. The results obtained are shown in the form of a Nyquist diagram. These impedance spectra were recorded after 1 hour of immersion in 1 M HCl at room temperature for different concentrations of MDYO and DYCD. These diagrams are shown in Fig. 5. The same

Fig. 5. Nyquist diagrams for stainless steel in 1M HCl solution containing various concentrations of the tested compounds: (a) MDYO and (b) DYCD (solid lines show fitted curve).

behavior was observed for both compounds and for all the concentrations studied. For high frequencies, HF, there was a wide capacitive loop followed by a short inductive loop at low frequencies, LF. Generally, the HF capacitive loop can be related to a load transfer from the corrosion process [51-53]. The inductive loop, LF, was attributed to the relaxation of adsorbed species such as acid anions (FeCl^-) for the blank solution and inhibitor species ($\text{FeCl}^- \text{inh}^+$) in the presence of inhibitor on the electrode surface [54-56]. The impedance diagrams obtained were not perfect capacitive half-loops, we have chosen the equivalent electrical circuit shown in Fig. 6. This circuit consisted of the electrolyte resistance (R_s), a constant phase element (CPE), used instead of the C_{dc} to account for the inhomogeneities of the electrode surface, positioned in parallel with a charge transfer resistance R_2 which is in turn in series with an inductance L_1 placed in

parallel with an inductive resistance. The experimental and simulated spectra were well correlated. The impedance of the constant phase element (CPE) is described by the following equation [57]:

$$Z_{CPE} = [Y_0(j\omega)^n]^{-1} \quad (21)$$

where Y_0 is the magnitude of CPE (a coefficient of proportionality), n is the phase shift of CPE, ω is the angular frequency and j is an imaginary unit. The value of the double-layer capacitance is obtained by the following equation [58]:

$$C_{dl} = Y_0(\omega_{\max})^{n-1} \quad (22)$$

Where $\omega_{\max} = 2\pi f_{\max}$, $f_{\max}$ is the frequency at which the imaginary value reaches a maximum. Inhibiting efficiency of corrosion is calculated from the values of R_{ct} according to the following relation-

Fig. 6. Equivalent electrical circuit used for simulating the impedance spectra.

ship [59]:

$$EI_{EIS}\% = \frac{R_{ct} - R_{ct}^o}{R_{ct}} \times 100 \quad (23)$$

where R_{ct} is the charge transfer resistance in presence of inhibitor and R_{ct}^o is the charge transfer resistance in blank solution.

The values of various impedance (electrochemical) parameters from this study are listed in Table 7. The examination of the latter showed that as the concentration of MDYO and DYCD increased in the corrosive medium (1 M HCl), R_{ct} increased in conjunction with a decrease in the value of the double-layer capacitance and Y_0 . These respective evolutions characterize, on the one hand, an increasing blocking of the charge transfer to the surface of the stainless steel due to the adsorbed inhibitor molecules forming a protective surface layer [51] and, on the other hand, a decrease in the contact surface related to the adsorption of the inhibitor. According to the Helmholtz model (Eq. 24), the decrease in C_{dl} values is mainly attributed to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer [60,61].

$$C_{dl} = \frac{\epsilon^o \epsilon S}{d} \quad (24)$$

Where d is the deposit thickness, ϵ^o is the permit-

Table 7. Electrochemical impedance parameters for the corrosion of 316 L SS immersed in 1 M HCl solutions in the absence and presence of various concentrations of MDYO or DYCD.

	C_{inh} (M)	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	Y_0 ($\mu \Omega \text{ s}^{-n} \text{ cm}^2$)	n	C_{dl} ($\mu \text{F cm}^2$)	L	R_l ($\Omega \text{ cm}^2$)	IE (%)
Blank	0	2.887	80.59	3924.1	0.69187	2454.37	88.2	18	-
MDYO	0.01×10^{-3}	2.206	226.4	451.47	0.74139	246.89	289.5	208.5	64.40
	0.05×10^{-3}	3.732	282.2	141.7	0.91631	112.13	777.1	182.8	71.44
	0.10×10^{-3}	2.745	366.3	187.33	0.87066	136.46	959.0	192.7	78.00
	0.50×10^{-3}	5.223	480.5	170.62	0.84539	118.94	543.0	246.3	83.23
	1.00×10^{-3}	4.477	666.5	121.38	0.91865	100.39	708.4	348.7	87.91
DYCD	0.01×10^{-3}	2.232	177.8	2838	0.64664	2207.28	361	85.39	54.67
	0.05×10^{-3}	2.314	290.8	770.26	0.69244	433.39	254.5	111.9	72.29
	0.10×10^{-3}	4.497	335.9	291.61	0.90804	237.81	371.1	151.1	76.01
	0.50×10^{-3}	2.545	387.1	174.86	0.93347	148.56	510.6	141.8	79.18
	1.00×10^{-3}	7.936	510.5	132.95	0.9058	105.55	1350	221.6	84.21

tivity of the medium, ε is the dielectric constant and S is the surface of the electrode.

Thus, the increase in the value of n with concentration, compared to that obtained for 1 M HCl, can be explained by a certain decrease in surface heterogeneity owing to the adsorption of the inhibitor at the best active adsorption sites [62].

In the presence of the two ketene dithioacetal derivatives, the inhibitory efficacy increased with concentration and reaches a maximum value of 87.91% in the case of MDYO at a concentration of 10^{-3} M. This compound performs better than CYDC. All the techniques used in this study such as weight loss, polarization curves, and electrochemical impedance spectroscopy show the same order of inhibitory efficacy MDYO > DYCD.

3.4. Surface investigation

Scanning Electron Microscopy has been widely used to analyze the morphological features of metal surfaces. Figs. 7 show the SEM images of polished stainless steel specimen surface taken before and after immersion in the corrosive mediums. We noted on the stainless steel surface picture before immersion (Fig. 7a) that this surface is smooth, homoge-

neous, and showed no sign of deformation whereas, after 3 hours of immersion at 25°C in 1M HCl alone (Fig. 7b), the surface was strongly damaged. On the other hand, the two images of the stainless steel surface, immersed for 3 h in 1 M HCl medium at 25°C in the presence of 1×10^{-3} M of MDYO and DYCD (Fig. 7c and d), show that the surfaces obtained new characteristics; and the damaged surface of the stainless steel was replaced by surfaces with better conditions. It was irregular as covered with a plate-like product in the case of MDYO (Fig. 7c), and seems more homogeneous compared to MDYO (Fig. 7d) reflecting the presence of an organic product. This observation indicates that the inhibition efficiency was due to the formation of an adherent deposit, less porous, stable, and insoluble which limited the access of the corrosive agent to the stainless steel surface. Similar observations were reported by P. Geethamani et al. [63], who attributed the deposition of the product to the creation of a protective film formed by adsorption of the inhibitors molecules on the metal surface.

To determine the nature of the adsorbed film, we used EDX which is considered an adequate method for this kind of characterization. Fig. 8 (a-d), shows the general EDX spectrum produced on the surface

Fig. 7. Micrographs (SEM) of the surface of stainless steel, (a) before immersion in 1M HCl, (b) after 3 h of immersion at 298 K in 1M HCl, after 3 hours of immersion at 298 K in HCl + 10^{-3} mol/L inhibitor, (c) MDYO, and (d) DYCD.

Fig. 8. EDX spectra of the surface of stainless steel (a) before immersion in 1 M HCl, (b) after 3 h immersion in 1M HCl at 298 K, after 3h immersion at 298 K in 1M HCl in the presence of 10^{-3} mol/L inhibitor, (c) MDYO, and (d) DYCD.

of stainless steel before immersion in the corrosive solution (1 M HCl) (Fig. 8a) and the general EDX spectrum obtained after 3 hours of immersion in 1 M HCl at 25°C (Fig. 8b), as well as (c) and (d) after 3 hours immersion in the corrosive media containing 10^{-3} M of the studied compounds (MDYO and DYCD, respectively), at 25°C. Examination of the

EDX spectra obtained reveals the presence of oxygen peaks. This suggests that oxides were formed by the reaction between the elements contained in the alloy (SS) and the oxygen present in the surrounding medium, air (Fig. 8a probably chromium oxide), or aqueous HCl solutions (Fig. 8 (b, c, d, and e probably iron oxides)). We also notice, after 3 hours of immer-

sion, the appearance of the chlorine peak, indicating the presence of this element on the surface. This presence is explained by the dissolution of the iron forming the iron chlorides [64] according to the following equation:

Fig. 8c and 8d, show the general EDX spectrum produced on the surface of stainless steel after 3 hours of immersion in a solution containing 1 M HCl + 10^{-3} M of MDYO and DCYCD respectively. A comparison of the atomic percentages obtained by EDX for the two compounds with the atomic percentage of stainless steel corroded in 1 M HCl (Table 8) clearly shows that the percentage of chlorine and oxygen decreases sharply in the presence of MDYO and DYCD. These observations confirm that these two compounds stop corrosion of the stainless steel by forming a layer that limits the access of the electrolyte to the surface. The increase in the atomic percentage of carbon and the appearance of the additional sulfur peak is an indication of the adsorption of the molecules of the two derivatives of ketene dithioacetal on the surface of stainless steel (Table 8). The low chlorine and oxygen content in the presence of MDYO indicates that this compound inhibits iron dissolution better than in the presence of DYCD, and the increase in the C and S contents in its presence has also demonstrated that MDYO can better adsorb on the surface of stainless steel, resulting in better inhibitory efficacy. This conclusion was also consistent with those of weight loss and electrochemical measurements.

3.5. Raman spectroscopy

Raman spectroscopic analysis was carried out to determine the corrosion products formed on the stain-

less steel surface under test. The Raman spectra performed on the stainless steel surface before immersion and after immersion in 1 M HCl and 1M HCl + 10^{-3} M inhibitor solution are shown in Fig. 9. It was noted that the spectrum obtained in the absence of the corrosive agent does not contain any peak (Fig. 9a), on the other hand, that obtained in the presence of 1 M HCl alone (Fig. 9b) was characterized by six, peaks that were observed at about 219 cm^{-1} , 283 cm^{-1} , 397 cm^{-1} , 489 cm^{-1} , 603 cm^{-1} , and at about 1301 cm^{-1} , these peaks correspond to Hematite ($\alpha\text{-Fe}_2\text{O}_3$), the peak observed at 665 cm^{-1} is attributed to Magnetite (Fe_3O_4) [65-67]. By comparing the Raman spectra performed on the stainless steel surface in the presence of HCl with and without inhibitors (MDYO and DYCD) (Fig. 9c and d), it is clear that the addition of inhibitors allowed the decrease of oxidation and corrosion of stainless steel. This was reflected by the absence of peaks corresponding to the corrosion products ($\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4), and by the appear-

Fig. 9. Raman spectra for stainless steel (a), in the presence of 1 M HCl (b) and after addition of MDYO (c) and DYCD (d).

Table 8. Element composition (atomic %) of SS surface after 3h immersion in 1M HCl without and with 1 mM MDYO and with 1mM DYCD derived from EDX analysis.

Elements (at. %)	Fe	C	O	S	Cl
Stainless steel polished	58.71	13.81	2.99	-	-
Stainless steel in 1 M HCl	52.38	18.04	7.37	-	0.88
Stainless steel in the presence of MDYO	54.29	19.29	3.54	0.37	0.15
Stainless steel in the presence of DYCD	54.55	18.07	4.41	0.23	0.25

ance of carbon certainly coming from the molecules of the inhibitors put in solution revealed by a large peak observed between 1200 to 1600 cm^{-1} . This study has shown that Hematite and Magnetite have been observed as the main corrosion products of the stainless steel studied, and it also confirms the results obtained by SEM/EDX which showed the presence of the molecules of these inhibitors, forming a protective layer on the surface of the stainless steel.

3.6. Computational Chemical Calculations

In this study, we have used several experimental methods to elucidate the corrosion-inhibiting capacity of stainless steel in acidic media by two ketene dithioacetal derivatives. The inhibitory properties are related to the interaction mechanism and the adsorption phenomena of these two molecules on the substrate surfaces. To obtain more information at the atomic scale, and to understand the mechanism of the corrosion inhibition of this metal by these two organic molecules, we have employed quantum-theoretical physicochemical methods for the studied these parameters. They are widely used in analyzing the reactivity of the molecules, in addition to the topology and electronic structure of the molecule/substrate systems [68,69] to define the adsorption modes and to qualify the types of interaction at the molecule/surface interface, to analyze and better control their physicochemical properties. To this end, we will present the results of this study, which allowed us to identify a certain number of structural and electronic parameters of the two inhibitors used in this work (Fig.10, Fig.11, Table 9, and Table 10). First, the optimized structures of MDYO and DYCD at CAM-B3LYP/311++G(d,p) level and the numbering of atoms as used in this work are given in Fig. 10. The energy of the highest occupied molecular orbital (E_{HOMO}) is often associated with the molecule's ability to donate electrons to a suitable vacant orbital. Thus, high HOMO energy values of the inhibitor indicate its tendency to yield electrons to an electron acceptor with unoccupied molecular orbital with low energy levels. Increasing E_{HOMO} values facilitate adsorption by influencing the transfer process through the adsorbed layer. However, the energy of the lowest unoccupied molecular orbital (E_{LUMO}) indicates the ability of the molecule to accept electrons. Therefore, a low value of E_{LUMO} means that the molecule indeed accepts electrons. The HOMO and LUMO electron density distribution

Fig. 10. Molecular structures of MDYO and DYCD compounds, and the numbering of atoms as used in this work.

Fig. 11. Optimized structures, HOMO and LUMO of the MDYO, and DYCD compounds at CAM-B3LYP/311++G(d,p) level.

of the molecules studied are shown in Fig. 11.

Thus, the HOMO density distribution is located on the heteroatoms (O, S) present in their structures for the two inhibitor molecules. On the other hand, the LUMO density is distributed over the chemical surface of both molecules. The calculated quantum parameters are summarized in Table 9. Examination of the E_{HOMO} energy values of both inhibitors suggests that the MDYO molecule has a greater tendency to donate electrons to the vacant orbital of acceptor substrate (higher E_{HOMO}) than the DYCD molecule. This result may explain the strong inhibition efficiency of MDYO observed experimentally. The energy difference between E_{LUMO} and E_{HOMO} (ΔE_{gap}) also supplies information about the reaction of inhibitor molecules. When ΔE_{gap} is low, the adsorption runs between inhibitors and metal surfaces increase because the energy required to remove an electron from the lowest occupied orbital will be

Table 9. Calculated quantum chemical parameters of the MDYO and DYCD compounds at CAM-B3LYP/311++G(d,p) level.

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{\text{(L-H)}}$ (eV)	χ (eV)	I (eV)	η (eV)	σ (eV) ¹	ΔN	Moment (D)
MDYO	-8.110	0.971	7.139	4.540	8.110	3.569	0.280	0.345	1.858
DYCD	-8.142	0.736	7.406	4.439	8.142	3.703	0.270	0.346	0.873

Table 10. Calculated atomic charges of MDYO and DYCD at CAM-B3LYP/311++G(d,p) level.

Mulliken			
Atoms	MDYO	Atoms	DYCD
C1	0.107	C1	0.088
S2	0.061	S2	0.072
C3	-0.222	C3	-0.212
S4	0.067	S4	0.071
C5	-0.268	C5	-0.245
C6	0.444	C6	0.276
O7	-0.441	O7	-0.431
O8	-0.266	C8	-0.141
O9	-0.419	C9	0.263
C10	0.290	C10	-0.120
C11	-0.281	O11	-0.425
C12	-0.210	C12	-0.197

low [70]. The absolute hardness (η) represents the variation of the chemical potential divided by the total number of atoms [71]. The higher the value of η , the more hard the compound, and the more difficult it is to participate in chemical reactions.

On the other hand, global softness (σ) is a quantitative characteristic of the polarization of electron clouds in compounds and it is the opposite of hardness [72]. The MDYO is highly reactive due to the lowest value of energy gap ($\Delta E_{\text{gap}} = 7.139$ eV), the highest value of softness ($\sigma = 0.280$ eV), and the lowest value of ionization potential ($I = 8.1010$ eV).), these properties make this compound more effective against metal corrosion due to its higher reactivity. It also has a higher electronegativity value ($\chi = 4.540$ eV), indicating that its molecule can attract electrons to form a covalent bond and can easily reach electron equilibrium. Inhibitor DYCD is characterized by the highest hardness value ($\eta = 3.703$ eV), implying that this molecule is resistant to electron change and,

therefore, tends to be less efficient than MDYO.

The dipole moment (μ) is a widely used parameter to describe the polarity of a molecule [73], and the total dipole moment only reflects the overall polarity of the molecule. It is clearly shown in the literature that molecules with high dipole moments are more reactive. The data pooled in Table 9 show that the MDYO inhibitor has a higher dipole moment than DYCD, which makes its inhibitory efficacy better. The calculation of the fraction of electrons transferred from the inhibitor to the metal surface (ΔN) was also performed in this study (Table 9). According to Lukovits' study [74], if the value of $\Delta N < 3.6$, the inhibitor's efficacy is considered good. In our case, the charge transfer rate is $\Delta N = 0.345$ eV for MDYO and $\Delta N = 0.346$ eV for DYCD and is below the limit value set by Lukovits. We concluded that each of these two compounds has an inhibiting effect against the corrosion of the metal. Mulliken's population analysis is used to identify inhibitor adsorption centers [75]. The more negatively charged the atoms of a molecule, the greater their ability to adsorb to the metal surface by a donor-acceptor interaction. The calculated data (Table 10) show that the oxygen atoms O(7) and O(9) in the MDYO molecule and the O(7) and O(11) atoms in the DYCD are the most negative, indicating that these atoms can act as adsorption centers via their free electron pair.

4. Conclusions

Two ketene dithioacetal derivatives, MDYO, and DCYD were synthesized and evaluated as possible corrosion inhibitors of type 316L stainless steel in 1 M HCl solution. The following conclusions are derived:

- Mass loss, potentiometry, and electrochemical impedance spectroscopy prove that corrosion of 316L stainless steel in 1M HCl media is reduced in the presence of different concentrations of MDYO and DYCD, and this inhibition increases with the

concentration of these two compounds.

- The inhibiting mechanism of adsorption inhibitor molecules on the surface of 316L stainless steel involves the blocking of the anodic and cathodic sites.

- The Nyquist diagram characterizes the adsorption of inhibitor molecules on 316L stainless steel.

- Scanning electron microscopy (SEM-EDX) and Raman spectroscopy corroborate these results.

- The mechanism of adsorption of both inhibitors involves physisorption.

- The apparent activation energy (E_a) of the metal dissolution and the high values of the standard free energy of adsorption ($\Delta G_{ads} > -20$ KJ/mol) verify the physisorption character of the more weighty adsorption.

- The adsorption process of these two molecules follows the Langmuir adsorption isotherm.

- Theoretical studies have revealed that the adsorption of these molecules can also occur directly via “donor-acceptor” bonds between the free electrons of heteroatoms (oxygen) and the vacant “d” orbitals of the iron atoms.

- The presence of the -OCH₃ group in the MDYO generates an electron-donor effect. This donor effect is not observable in the case of DYCD, which promotes the adsorption of MDYO more than DYCD.

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