



# Inhibition properties of self-assembled corrosion inhibitor talloil diethylenetriamine imidazoline for mild steel corrosion in chloride solution saturated with carbon dioxide



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## ABSTRACT

The inhibition effect of talloil diethylenetriamine imidazoline (TOFA/DETA imidazoline) on corrosion of mild steel in chloride solutions saturated with CO<sub>2</sub> was investigated by weight loss measurements (WL) and atomic force microscopy (AFM). Adsorption mechanism and kinetics of self-assembled (TOFA/DETA imidazoline) monolayers formation on gold were studied using the quartz crystal microbalance measurements (QCM). WL and AFM results demonstrated that TOFA/DETA imidazoline can effectively protect mild steel surface from corrosion. QCM measurements shown that the adsorption of TOFA/DETA imidazoline onto gold follows Langmuir adsorption isotherm and further investigation of the adsorption process will be carried out on a corroding metal surface.

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## 1. Introduction

Corrosion caused by CO<sub>2</sub> in aqueous phase is a major problem encountered in multiphase carbon steel pipelines used in oil and gas industry. One of the most practical methods for protection of carbon steels exposed to CO<sub>2</sub>, mainly due to economical reasons, is the addition of organic substances as corrosion inhibitors [1–3]. Investigation of corrosion inhibition mechanism by adsorption of inhibitor on the metal surface is very difficult due to the complexity of chemical structure of inhibitors used in petroleum industry. Low concentrations at which these inhibitors are used as well as the diversity of the environment surrounding the inhibitor under real conditions make this research especially challenging [4]. Corrosion inhibitors contain different functional groups, usually polar head (fatty acids, amines, imidazolines, oxyalkylated amines, oxygen, sulfur or phosphorus containing species, quaternary amines) and long hydrocarbon chain (typically C<sub>14</sub>–C<sub>18</sub>), which promote the binding of inhibitor molecules to the metal surface [5–10]. Imidazolines are widely used in oil industry as corrosion inhibitors, but their properties and behavior are not yet fully known. They are classified as cationic surfactants with positive charge on imidazoline nucleus, which is unaffected by change in pH of the environment, thereby easily adsorbed on the metal surface, which is negatively charged [11]. It is of great importance to determine which functional groups bind to the metal in order to gain better understanding of the corrosion inhibition mechanism.

Imidazolines are organic compounds with two nitrogen atoms in the heterocycle and three different sites suitable for bonding: pyridine like nitrogen atom N3, pyrrole like nitrogen atom N1 and aromatic ring [12]. Some modeling studies propose that the head and the pendent groups enable bonding of the inhibitor molecules to the metal surface while the hydrocarbon tail limits the transport of corrosive species from solution to the metal surface and forms the monolayer. These corrosion inhibitors are believed to form self-assembled films that protect the steel surface against corrosion [13]. Self-assembled systems are ordered molecular assemblies formed spontaneously by the adsorption of an active surfactant molecules on a solid surface, as a result of competing intermolecular, molecules–substrate and molecules–solvent interactions [14,15]. Because of the surfactant properties of corrosion inhibitors, when dissolved in a solution the free energy of the system increases resulting in the corrosion molecules concentrating at the solution interface. The surfactant molecules accumulate favorably at the solution/air interface and consequently the surface tension decreases. The surface tension continues to fall as the surfactant concentration increases until the critical micelle concentration (CMC) is attained. The shape and size of a micelle is defined by surfactant nature, concentration, temperature, pH, and ionic strength of the solution. The full coverage of the exposed metal surface by protective inhibitor film is usually established after saturation of the surfactant molecules in the medium [16]. Some studies have shown that inhibitor solutions at concentrations greater than the CMC are more effective in corrosion protection than solutions at concentrations below the CMC [17].

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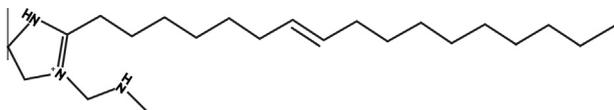


Fig. 1. Molecular structure of TOFA/DETA imidazoline.

In our previous study [10] the inhibition effect of TOFA/DETA imidazoline for mild steel corrosion in 3 wt% NaCl saturated with CO<sub>2</sub> was investigated at 20 °C and 70 °C, pH 5, without and with 70 ppm<sub>v</sub> of TOFA/DETA imidazoline using linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic sweep measurements (PDS). The results shown that the corrosion rate decreased from 1 mm y<sup>-1</sup> for bare steel to 0.1 mm y<sup>-1</sup> when 70 ppm<sub>v</sub> of TOFA/DETA imidazoline was added and from 4 mm y<sup>-1</sup> for bare steel to 0.2 mm y<sup>-1</sup> by adding 70 ppm<sub>v</sub> of TOFA/DETA imidazoline at 70 °C. To further confirm these findings, in the present study we investigated the inhibition effect of TOFA/DETA imidazoline for mild steel corrosion in 3 wt.% aqueous NaCl solution saturated with CO<sub>2</sub> using weight loss measurements, while the surface morphology of mild steel in the presence and absence of TOFA/DETA imidazoline was studied by atomic force microscopy (AFM). The focus of our current research was the investigation of mechanism and kinetics of TOFA/DETA imidazoline adsorption onto gold from 3 wt.% aqueous NaCl solution saturated with CO<sub>2</sub> using the quartz crystal microbalance (QCM). Low reactivity and surface roughness of gold and its affinity towards nucleophiles centres makes gold coated quartz crystals, as a model surface, very suitable for the investigation of the influence of temperature and inhibitor concentration on the adsorption process. This procedure may not be completely adequate since knowledge gained from gold surface may not be directly applicable to mild steel surface. However well defined and characterized model surfaces are needed in order to successfully study corrosion inhibitor adsorption. Further advances in this research would be greatly supported by the obtained results that would be used to check and evaluate the corrosion inhibitor adsorption on steel surface as well.

Molecular structure of TOFA/DETA imidazoline, as shown in Fig. 1, is comprised of long-chain nitrogenous surfactant and its properties at the solution/air interface were investigated by measuring the surface tension using the drop count method. Further investigation was conducted by fitting the experimental data with analytical equations in order to define the adsorption isotherm and to calculate the thermodynamic parameters.

## 2. Materials and methods

### 2.1. Corrosion measurements

The carbon steel API X65 was used in all corrosion measurements. The X65 carbon steel composition is shown in Table 1.

Weight-loss specimens, circular disks with an exposed area of 7.5 cm<sup>2</sup>, were sequentially grinded using 240, 320, 400 and 600 grit silicon carbide paper, rinsed with isopropanol in an ultrasonic cleaner for 1–2 min and then air-dried. The cleaned samples were weighed before immersion of the specimen into the 3 wt.% NaCl

Table 2  
Experimental conditions for corrosion measurements.

Parameters	Conditions
Total pressure (bar)	1
Test solution	3 wt.% NaCl
Solution volume, dm <sup>3</sup>	1.8
Corrosion inhibitor	TOFA/DETA imidazoline
Inhibitor concentration (ppm <sub>v</sub> )	0, 70
Liquid temperature (°C)	20, 70
pH	5
Measurements	Weight loss

purged with CO<sub>2</sub> gas without and with 70 ppm<sub>v</sub> of TOFA/DETA imidazoline at 20 °C, and at 70 °C. The cell temperature was followed by a thermocouple. When the required temperature was achieved, the pH of the test solution was adjusted to 5 by addition of a deoxygenated sodium bicarbonate solution. After 24 h the samples were then taken out of the solution rinsed with isopropanol, wiped with a cloth, then air dried and accurately weighed on an analytic balance (accuracy ± 0.1 mg). The test matrix for this experimental series is shown in Table 2.

### 2.2. Surface morphology

The analysis of the morphology of the mild steel surface was carried out using atomic force microscopy (AFM), operated in the contact mode under ambient conditions, at a scan rate 0.7 Hz, scan angle 0, scan points 256 and scan lines 256 using an MFP-3d Standing Alone AFM instrument, Asylum Research, Inc. Images of the specimens were recorded after 24 h exposure time in 3 wt.% NaCl purged with CO<sub>2</sub> gas at 20 °C, and at 70 °C without and with 70 ppm<sub>v</sub> of TOFA/DETA imidazoline. The purpose of investigating the topography of the surface was to characterize the surface roughness on a microscale.

### 2.3. Determination of CMC value using the drop count method

In this research the measurement of the surface tension of 3 wt.% aqueous NaCl solution in the absence and presence of various concentrations of TOFA/DETA imidazoline was performed using drop count method. All the experiments were carried out at 20 °C, pH 5. In order to determine the critical micelle concentration (CMC) for corrosion inhibitor TOFA/DETA imidazoline the surface tension was measured in the concentration range from 10 ppm<sub>v</sub> to 90 ppm<sub>v</sub>.

### 2.4. QCM measurements

All the adsorption measurements were carried out using a quartz crystal microbalance (QCM) Stanford Research Systems, Model QCM200, USA in a glass cell shown in Fig. 2. The quartz crystal microbalance is a simple, high-resolution mass sensing technique, based upon the piezoelectric effect. The device included a controller, a crystal oscillator, a crystal holder and quartz crystals (2.54 cm diameter, AT-cut Stanford Research Systems) coated with sputtered gold. The frequency of the used crystals was 5 MHz. Prior to use, gold coated quartz crystals were cleaned for 2 min in

Table 1  
Chemical composition of X65 mild steel (mass% balance is Fe).

Al	As	B	C	Ca	Co	Cr	Mn	Mo	Ni	Nb
0.032	0.008	0.001	0.13	0.002	0.007	0.14	1.16	0.16	0.36	0.017
P	Pb	S	Sb	Si	Sn	Ta	Ti	V	Zr	Cu
0.009	<0.001	0.009	0.009	0.26	0.007	<0.001	<0.001	0.047	<0.001	0.131

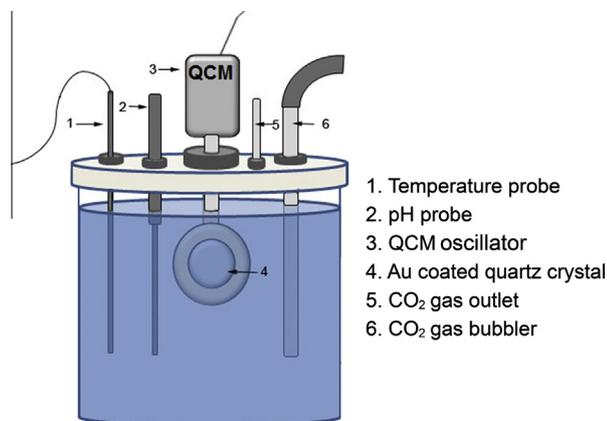


Fig. 2. Experimental setup for QCM measurements.

piranha solution (1:3 by volume of 30%  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ ) rinsed with distilled water and isopropanol, and dried under a stream of nitrogen. The purity of the crystals after cleaning procedure was ensured by checking their frequency response in air. The solution was stirred (150 rpm) and the cell temperature was monitored by a thermocouple. When temperature was achieved, the pH of the test solution was adjusted to 5 by adding a deoxygenated sodium bicarbonate solution.

Corrosion inhibitor TOFA/DETA imidazoline was adsorbed onto gold coated quartz crystals from 3 wt.% aqueous NaCl solution. The solutions were deoxygenated by purging  $\text{CO}_2$  gas for 1 h before the start of each experiment and during the whole test in order to maintain positive  $\text{CO}_2$  partial pressure. Experiments were performed at the following temperatures: 20 °C, 25 °C, 30 °C and 35 °C. Data was collected over inhibitor concentration range from 50 ppm<sub>v</sub> to 90 ppm<sub>v</sub>. Once the desired conditions were achieved the QCM holder was immersed into the solution. The test matrix for this experimental series is shown in Table 3.

### 3. Results and discussions

#### 3.1. Weight loss measurements

The effect of addition of the TOFA/DETA imidazoline inhibitor on the corrosion of mild steel in 3 wt.% NaCl solution was studied by weight loss measurements at 20 °C and 70 °C after a 24 h immersion period. The weight loss method was used in order to estimate average corrosion rates. The weight loss ( $W_L$ ) was calculated as follows:

$$W_L = W_1 - W_2 \quad (1)$$

where  $W_1$  and  $W_2$  are the average weight of the specimens before and after exposure, respectively. The corrosion rate,  $v_{\text{corr}}$ , was calculated using the equation:

$$v_{\text{corr}} = \frac{W_L}{t\rho S} \quad (2)$$

Table 3

Experimental conditions for QCM measurements.

Parameters	Conditions
Total pressure (bar)	1
Test solution	3 wt.% NaCl
Corrosion inhibitor	TOFA/DETA imidazoline
Inhibitor concentration (ppm <sub>v</sub> )	50, 60, 70, 90
Liquid temperature (°C)	20, 25, 30, 35
pH	5
Measurements	QCM

Table 4

Weight loss measurements after 24 h for mild steel in 3 wt.% NaCl solution without and with inhibitor TOFA/DETA imidazoline, at 20 °C and 70 °C.

Solution	$\Delta W$ (mg)	$v_{\text{corr}}$ (mm y <sup>-1</sup> )	$\eta$ (%)
3 wt.% NaCl, 20 °C	0.0182	1.05	–
3 wt.% NaCl, $c_{\text{inh}} = 70$ ppm <sub>v</sub> , 20 °C	0.0003	0.017	98.4
3 wt.% NaCl, 70 °C	0.0780	4.53	–
3 wt.% NaCl, $c_{\text{inh}} = 70$ ppm <sub>v</sub> , 70 °C	0.0045	0.26	94.3

where  $S$  is the surface area of specimens,  $\rho$  is the density of iron and  $t$  is the exposure time. Using the obtained results from weight loss measurements, the inhibition efficiency,  $\eta$ , was determined by the following equation:

$$\eta = \frac{v_{\text{corr}} - v_{0\text{corr}}}{v_{0\text{corr}}} \times 100\% \quad (3)$$

where  $v_{\text{corr}}$  and  $v_{0\text{corr}}$  are the mild steel corrosion rates with and without TOFA/DETA imidazoline, respectively [18]. It can be seen from Table 4 that the corrosion rate significantly decreased after the addition of TOFA/DETA imidazoline corrosion inhibitor at both temperatures, while the inhibition efficiency was calculated to be around 95%. The high inhibition efficiency can be explained by the adsorption of TOFA/DETA imidazoline on the mild steel surface. The results obtained from the weight loss measurements are in accordance with the previously obtained results from the electrochemical measurements [10].

#### 3.2. Surface morphology

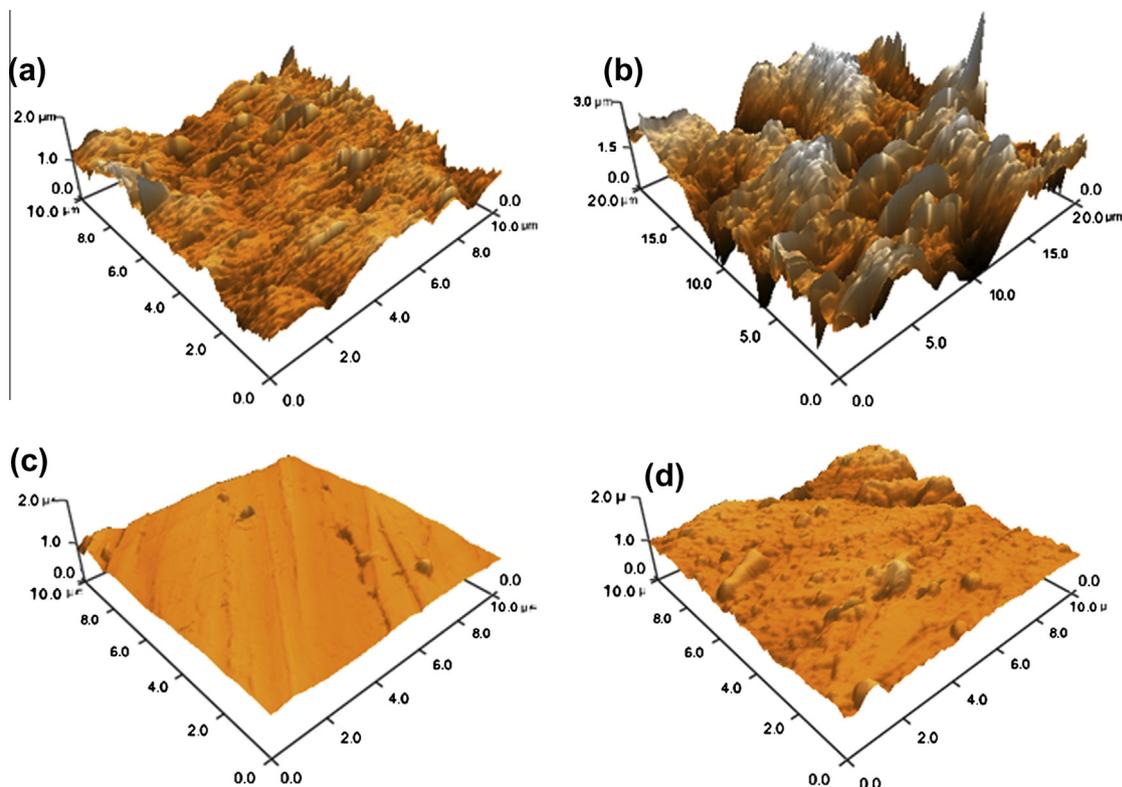
Further investigation of the corrosion resistance ability of TOFA/DETA imidazoline films was carried out by means of atomic force microscopy (AFM) in order to characterize the mild steel surface microstructure. The three-dimensional AFM images of mild steel surface after 24 h of exposure to 3 wt.% NaCl solutions without and with TOFA/DETA imidazoline at 20 °C and at 70 °C are shown in Fig. 3. In the absence of inhibitor (Fig. 3a and b), the mild steel surface was strongly damaged due to metal dissolution in the corrosive solution. Nevertheless, the appearance of steel surface was significantly different after the introduction of TOFA/DETA imidazoline to the corrosive solution. Fig. 3c and d clearly shows that the corrosion rate of mild steel decreased and very flat surface appeared, suggesting that TOFA/DETA imidazoline forms an inhibitive film on the mild steel surface.

The graphs of the average height of the entire image (the average of 512 line profiles across the scanned area) of the mild steel surface in the presence and absence of TOFA/DETA imidazoline shown in Fig. 4 were given to show general height variation.

The value of surface roughness ( $RMS$ ), derived from AFM height profile images (Fig. 4), for the bare steel after exposure at 20 °C was 165 nm, while the  $RMS$  value after exposure at 70 °C significantly increased to 712 nm. In the presence of 70 ppm<sub>v</sub> TOFA/DETA imidazoline the  $RMS$  value at 20 °C was 42 nm, while at 70 °C  $RMS$  value was 97 nm due to the formation of inhibitor film on the mild steel surface, which causes the decrease of the steel surface roughness and effectively protects mild steel from corrosion. The AFM results are in a good agreement with the weight loss results and electrochemical measurements [10].

#### 3.3. Determination of CMC value using drop count method

The values of the surface tension determined using the drop count method for different concentrations of corrosion inhibitor in 3 wt.% NaCl saturated with  $\text{CO}_2$  are shown in Fig. 5. The CMC concentration corresponds to the point where the surfactant first



**Fig. 3.** Atomic force microscopy three-dimensional images of mild steel surface in 3 wt.% NaCl saturated with CO<sub>2</sub> (a) without inhibitor at 20 °C, (b) without inhibitor at 70 °C, (c) containing 70 ppm<sub>v</sub> TOFA/DETA imidazoline at 20 °C and (d) containing 70 ppm<sub>v</sub> TOFA/DETA imidazoline at 70 °C.

shows the lowest surface tension, and after this point the surface tension remains relatively constant.

As it can be seen in Fig. 5 the increase in inhibitor concentration leads to the accumulation of inhibitor at the solution/air interface and consequently decreases the value of the surface tension of the solution. TOFA/DETA imidazoline has been found to have CMC value of 65 ppm<sub>v</sub> in 3 wt.% aqueous NaCl solution saturated with CO<sub>2</sub> at 20 °C, pH 5. It should be taken into account that CMC value depends on the pH of the solution and its ionic strength.

#### 3.4. The use of QCM for determination of thermodynamic parameters of adsorption

The QCM is a mass sensing device which is used to measure the frequency shift caused by a small mass changes in the region near the QCM solution interface. In this research the change of the oscillation frequency of the QCM,  $\Delta f$ , was recorded after TOFA/DETA imidazoline was added in the 3 wt.% NaCl solution in a very dilute solution state (from 50 ppm<sub>v</sub> to 90 ppm<sub>v</sub> which is close to CMC value of 65 ppm<sub>v</sub>). The correlation between mass and frequency is described by the Sauerbrey equation, as shown following, which is a linear relationship [19].

$$\Delta f = - \frac{2f_0^2}{\sqrt{\mu_q \rho_q}} \Delta m \quad (4)$$

where  $\Delta f$  is the frequency change,  $\Delta m$  is the change in mass per unit area,  $f_0$  is the resonant frequency of the fundamental mode of the crystal,  $\mu_q$  is the shear modulus of quartz and  $\rho_q$  is the density of quartz. The obtained time dependence of frequency change is a direct result of the formation of inhibitor film. As expected, the frequency change was found to decrease continuously with the observation time. The frequency decreased and the exponential mass increase indicated the presence of an adsorbed inhibitor layer at

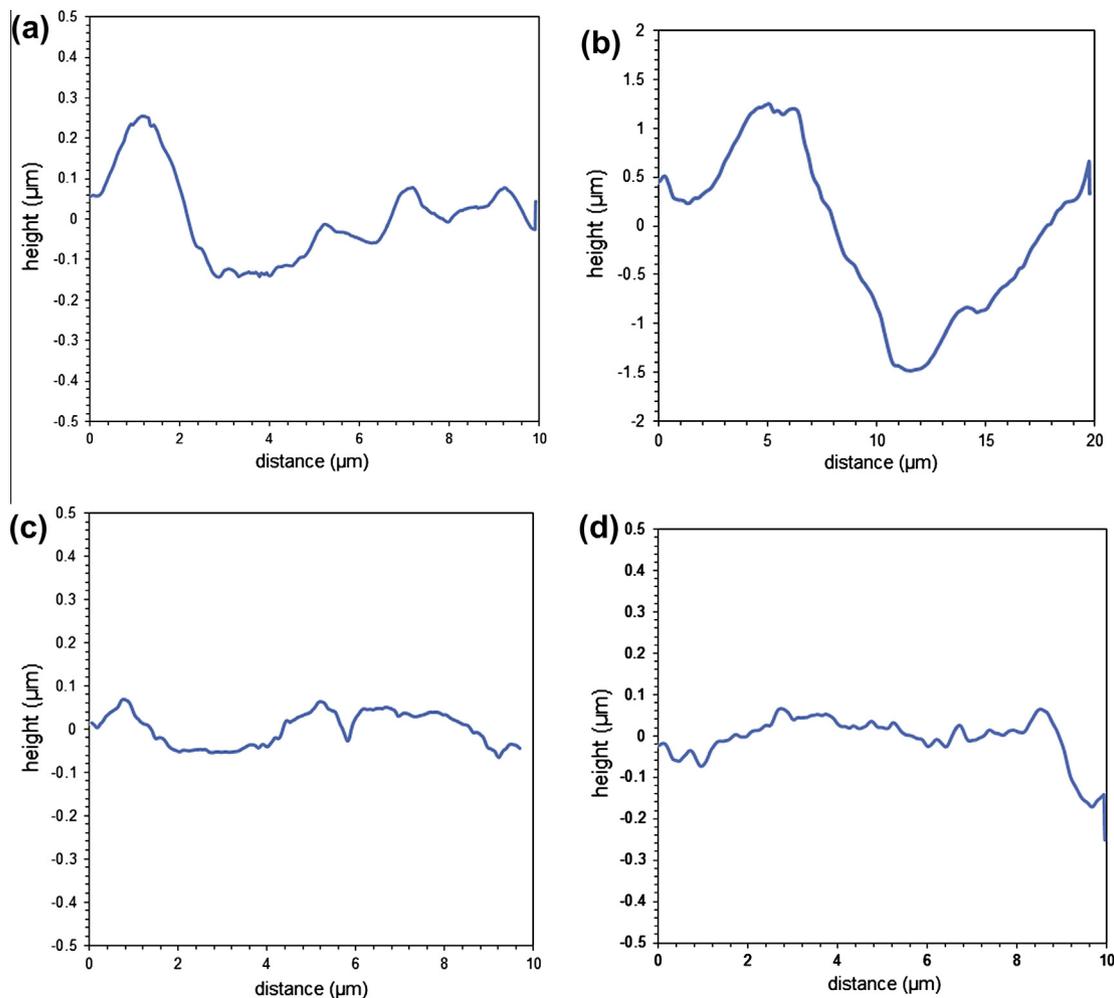
the gold coated quartz crystal surface. The equilibrium was achieved within a certain period of time following the TOFA/DETA imidazoline introduction. The TOFA/DETA imidazoline molecule contains two nitrogen atoms and p-electrons which enable the molecule to be adsorbed on the metal surface via lone-pair electrons [20].

Obtained experimental data (Fig. 6) indicate that the Langmuir adsorption isotherm can be used to describe the kinetics of adsorption process over a concentration range close to CMC value. While, formed horizontal plateau corresponds to the formation of a monolayer of TOFA/DETA imidazoline on a gold coated quartz crystal surface. According to the literature monolayers insoluble in water are only formed when alkyl chain consists of at least 12 carbon atoms [21]. These n-alkyl chains are oriented perpendicular to the water surface while the hydrophilic head group is submerged into the water phase [22]. Obtained experimental data was fitted to the Langmuir adsorption model, since the Langmuir isotherm is based on the assumption that the adsorption process is limited to one monolayer, consequently the obtained time dependence of frequency change is a direct result of the formation of the inhibitor monolayer [23,24]. Since the frequency change depends on the surface coverage, which is defined as the ratio between occupied sites and available sites on the surface, the rate of surface reaction can be described using the following equation:

$$\frac{d\theta}{dt} = k_a(1 - \theta)c - k_d\theta \quad (5)$$

where  $\theta$  is the surface coverage,  $c$  is inhibitor concentration,  $k_a$  and  $k_d$  are the adsorption and desorption constants, respectively. Integration of this equation gives the time course of the monolayer formation:

$$\theta(t) = K'[1 - \exp(-kt)] \quad (6)$$

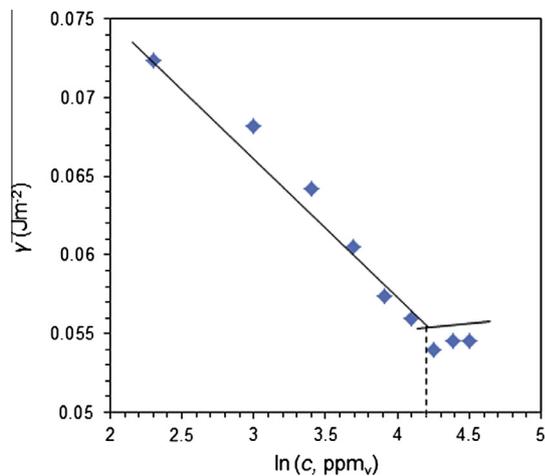


**Fig. 4.** Graphs of the average height of the entire image profiles of mild steel surface in 3 wt.% NaCl saturated with CO<sub>2</sub> (a) without inhibitor at 20 °C, (b) without inhibitor at 70 °C, (c) containing 70 ppm<sub>v</sub> TOFA/DETA imidazoline at 20 °C and (d) containing 70 ppm<sub>v</sub> TOFA/DETA imidazoline at 70 °C.

where  $k$  and  $K'$  are the constants presented by the following equations, respectively:

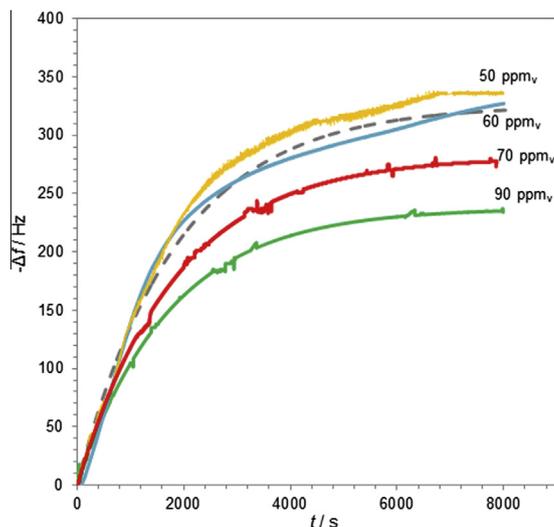
$$k = k_a c + k_d \tag{7}$$

$$K' = \frac{c}{\left(c + \frac{k_d}{k_a}\right)} \tag{8}$$



**Fig. 5.** Dependence of surface tension,  $\gamma$ , on TOFA/DETA imidazoline concentration,  $\ln c$ , in 3 wt.% NaCl saturated with CO<sub>2</sub>.

In Fig. 6 the time dependences of frequency change,  $\Delta f$  for different concentrations of TOFA/DETA imidazoline at 20 °C are shown in solid lines while the dashed line represents the



**Fig. 6.** Frequency change,  $\Delta f$ , of QCM for different concentration of TOFA/DETA imidazoline in 3 wt.% NaCl saturated with CO<sub>2</sub> on a gold surface, pH 5, 20 °C (solid lines – experimental, dashed line – fitting for the concentration of 60 ppm<sub>v</sub> of TOFA/DETA imidazoline).

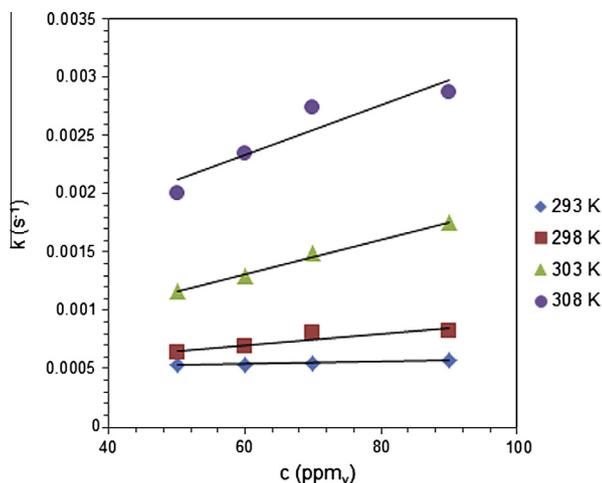


Fig. 7. The concentration dependence of  $k$  for TOFA/DETA imidazoline in 3 wt.% NaCl solution saturated with  $\text{CO}_2$ , at different temperatures.

corresponding curve obtained by fitting the experimental data to Langmuir adsorption isotherm for the concentration of 60 ppm<sub>v</sub> of TOFA/DETA imidazoline. The fit obtained at this concentration shows that the proposed model is in a good accordance with the recorded experimental data. The fitting procedure was repeated for all the temperatures from 20 °C to 35 °C (data not shown).

As it can be seen in Fig. 6 the required exposure time to reach the steady state at each concentration decreased with increasing TOFA/DETA imidazoline concentration. The concentration dependence of  $k$  for TOFA/DETA imidazoline in 3 wt.% NaCl solution saturated with  $\text{CO}_2$  at different temperatures obtained by fitting the experimental data to the Langmuir adsorption model Eq. (6) is shown in Fig. 7.

From the slopes and intercepts of the lines in Fig. 7 the values of the adsorption and desorption constants,  $k_a$  and  $k_d$ , for monolayer assembly formation have been calculated according to Eq. (7) and presented in Table 5.

It can be observed from Table 5 the positive value of desorption constant,  $k_d$ , for TOFA/DETA imidazoline adsorption indicates the equilibrium process while the adsorption constant,  $k_a$ , increases with increase in temperature, and consequently, the time required to reach saturation is shorter. This is evident as shown by the lines in Fig. 8, where we compare the obtained fits of Langmuir adsorption isotherms for experimental data recorded after the injection of 50 ppm<sub>v</sub> of TOFA/DETA imidazoline in 3 wt.% NaCl solution saturated with  $\text{CO}_2$  at different temperatures.

As it can be seen in Fig. 8 time required to reach equilibrium state decreased at higher temperatures. The obtained results indicate that the adsorption of TOFA/DETA imidazoline from 3 wt.% NaCl solution saturated with  $\text{CO}_2$  onto gold coated quartz crystal is an endothermic reaction since an increase in temperature drives an endothermic reaction forward to products. The required time to reach saturation decreased from approximately 100 min at 293 K to 30 min at 308 K. Standard adsorption equilibrium constant,

Table 5  
The values of adsorption constant,  $k_a$  and desorption constant,  $k_d$  at different temperatures.

$t$ (°C)	$k_a$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$k_d$ ( $\times 10^{-4} \text{s}^{-1}$ )
20	1.63	4.69
25	6.81	4.67
30	10.70	7.98
35	29.98	10.47

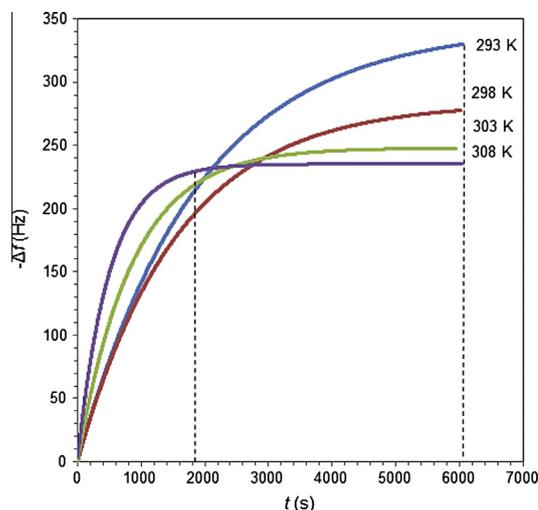


Fig. 8. The frequency change,  $\Delta f$ , in the presence of TOFA/DETA imidazoline in 3 wt.% NaCl solution at a concentration of 50 ppm<sub>v</sub> at different temperatures.

$K_{\text{eq}}$ , and standard Gibbs free energy of adsorption,  $\Delta G_{\text{ads}}^0$ , were determined from the following equations, respectively:

$$K_{\text{eq}} = \frac{k_a}{k_d} \quad (9)$$

$$\Delta G_{\text{ads}}^0 = -RT \ln K_{\text{eq}} \quad (10)$$

where  $R$  is the gas constant and  $T$  is the absolute temperature. Calculated values of  $K_{\text{eq}}$  and  $\Delta G_{\text{ads}}^0$  determined from collected data are summarized in Table 6.

It can be noticed from Table 6 that the standard adsorption equilibrium constant increases with temperature, suggesting that the higher temperature accelerates the adsorption of TOFA/DETA imidazoline, therefore, the adsorption of the inhibitor increases with the temperature increase. The negative values of  $\Delta G_{\text{ads}}^0$  as recorded in Table 6 indicate that the adsorption of TOFA/DETA imidazoline from 3 wt.% NaCl solution saturated with  $\text{CO}_2$  onto gold coated quartz crystals is spontaneous and favorable. The values of  $\Delta G_{\text{ads}}^0$  around  $-20 \text{ kJ mol}^{-1}$  or less negative indicate physisorption, electrostatic interactions between the inhibitor and the metal surface, while the values around  $-40 \text{ kJ mol}^{-1}$  or more negative are seen as chemisorption, which is due to the charge sharing between inhibitor molecules and the metal surface [25–27]. In the present work, the calculated values of  $\Delta G_{\text{ads}}^0$  at different temperatures are higher than  $-40 \text{ kJ mol}^{-1}$  but lower than  $-20 \text{ kJ mol}^{-1}$ , which indicates that adsorption of TOFA/DETA imidazoline is governed by both chemisorption and physisorption mechanism. The temperature dependence of  $K_{\text{eq}}$  allows the calculation of the standard enthalpy of adsorption,  $\Delta H_{\text{ads}}^0$ , using the van't Hoff equation [28,29].

$$\ln K_{\text{eq}} = -\frac{\Delta H_{\text{ads}}^0}{RT} + \text{constant} \quad (11)$$

Table 6  
The values of  $K_{\text{eq}}$  and  $\Delta G_{\text{ads}}^0$  determined from collected data as a function of temperature.

$t$ (°C)	$T$ (K)	$K_{\text{eq}}$ ( $\times 10^3 \text{M}^{-1}$ )	$\Delta G_{\text{ads}}^0$ ( $\text{kJ mol}^{-1}$ )
20	293	3.476	-19.86
25	298	14.58	-23.75
30	303	13.41	-23.94
35	308	28.63	-26.28

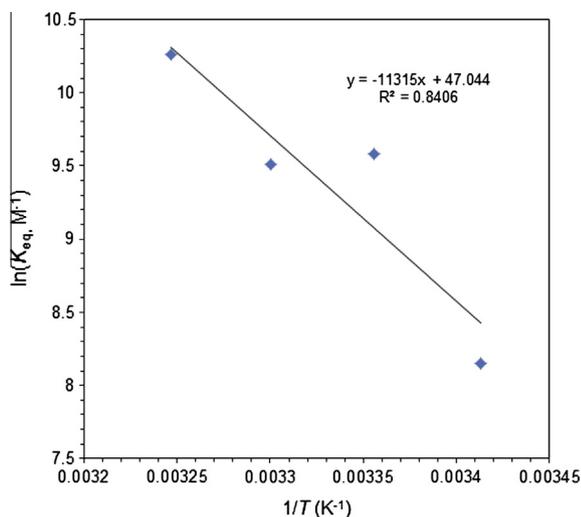


Fig. 9. Van't Hoff plot for adsorption of TOFA/DETA imidazoline in the temperature range from 293 K to 308 K.

Van't Hoff plot for adsorption of TOFA/DETA imidazoline in the temperature range from 293 K to 308 K is shown in Fig. 9, where, the negative slope indicates an endothermic adsorption process, meaning that the equilibrium constant increases, as the temperature increase. The value of  $\Delta H_{\text{ads}}^0$  was calculated to be  $94.07 \text{ kJ mol}^{-1}$ , which is in agreement with the results presented in Fig. 8, where we have shown that time required to reach equilibrium state decreased at higher temperatures.

In order to determine standard entropy of adsorption at any given temperature, the change in standard Gibbs free energy of adsorption,  $\Delta G_{\text{ads}}^0$ , may be written from the definition of the Gibbs free energy as [30]:

$$\Delta G_{\text{ads}}^0 = \Delta H_{\text{ads}}^0 - T\Delta S_{\text{ads}}^0 \quad (12)$$

The temperature dependence of  $\Delta G_{\text{ads}}^0$  for adsorption of TOFA/DETA imidazoline in the temperature range from 293 K to 308 K is shown in Fig. 10.

The value of  $\Delta S_{\text{ads}}^0$  was calculated to be  $0.389 \text{ kJ mol}^{-1} \text{ K}^{-1}$ , while  $\Delta H_{\text{ads}}^0$  was  $93.44 \text{ kJ mol}^{-1}$ , that is in agreement with the value of  $\Delta H_{\text{ads}}^0$ , obtained using the van't Hoff equation. Although it is commonly believed that simple adsorption on bare surface is generally an exothermic process which is followed by a decrease in entropy [31,32], the obtained positive value of  $\Delta H_{\text{ads}}^0$  and the positive value of  $\Delta S_{\text{ads}}^0$  indicate that the adsorption process of TOFA/DETA imidazoline on a gold surface is endothermic and driven by entropy gain associated with the breaking down of inhibitor structures formed in the bulk. It has been proven that local electron densities or charges are important in many chemical reactions and physico-chemical properties of inhibitor compound [33]. According to molecular structure of TOFA/DETA imidazoline (Fig. 1) N1 atom in imidazoline ring and N atom in the pendent group carry negative charges, therefore adsorb on the oppositely charged hydrophilic gold surface through the electrostatic interactions, followed by desorption of small molecules or ions such as  $\text{H}_2\text{O}$  and  $\text{Cl}^-$  from the gold surface. The adsorption study on inert, non-corroding substrate provides useful information for the further investigation of adsorption process on a corroding metal surface. Additional experiments will be carried by means of QCM on iron coated quartz crystals in order to investigate the mechanism of adsorption of TOFA/DETA imidazoline on a real corroding metal surface, since it is reported that the inhibitor adsorption on corroding surfaces never reaches the real equilibrium and tends to an

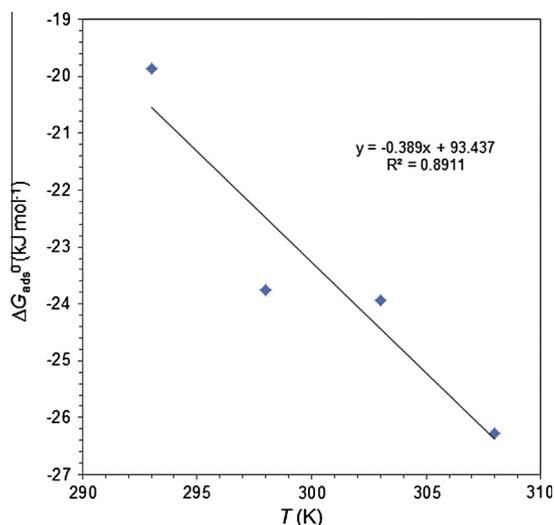


Fig. 10. Temperature dependence of  $\Delta G_{\text{ads}}^0$  for adsorption of TOFA/DETA imidazoline in the temperature range from 293 K to 308 K.

adsorption steady state, whereas the potential and the surface changes with time should be also considered [34].

#### 4. Conclusions

The inhibition effects of talloil diethylenetriamine imidazoline (TOFA/DETA imidazoline) on the corrosion of mild steel in 3 wt.% NaCl solution saturated with  $\text{CO}_2$  was further studied using weight loss measurements and AFM surface analysis, while the focus of our research was the investigation of mechanism and kinetics of TOFA/DETA imidazoline adsorption onto gold. Weight loss measurements shown that the addition of the TOFA/DETA imidazoline inhibitor to 3 wt.% NaCl solution significantly reduced the corrosion rate, while the inhibition efficiency was calculated to be around 95%. The inhibition effect of TOFA/DETA imidazoline was further confirmed by AFM measurements, where it was shown that TOFA/DETA imidazoline decreases the steel surface roughness and effectively protects mild steel from corrosion due to the formation of the inhibitor film. QCM measurements confirmed that TOFA/DETA imidazoline forms self-assembled monolayers on gold coated quartz crystals. Gold surface was employed as well defined and characterized model surface in order to successfully study TOFA/DETA imidazoline adsorption. It is shown that adsorption kinetics of this self-assembled system can be described by Langmuir adsorption isotherm. The obtained values of  $\Delta G_{\text{ads}}^0$  at different temperatures indicate that adsorption of TOFA/DETA imidazoline on the gold surface is spontaneous and favorable governed by both chemisorption and physisorption mechanism. The entropy of adsorption,  $\Delta S_{\text{ads}}^0$ , was calculated to be  $0.389 \text{ kJ mol}^{-1} \text{ K}^{-1}$ , while the enthalpy of adsorption,  $\Delta H_{\text{ads}}^0$ , was around  $94 \text{ kJ mol}^{-1}$ . TOFA/DETA imidazoline adsorbs on the oppositely charged hydrophilic gold surface through the electrostatic interactions, between the TOFA/DETA imidazoline head group or pendent group and the gold surface active sites, followed by desorption of small molecules or ions such as  $\text{H}_2\text{O}$  and  $\text{Cl}^-$ . The study by QCM of imidazoline adsorption on gold coated quartz crystal is only for process modeling, the obtained results are not of direct relevance for imidazoline adsorption on steel. Additional experiments will be carried by means of QCM on iron coated quartz crystals in order to investigate the mechanism of adsorption of TOFA/DETA imidazoline on a real corroding metal surface.

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