Anal. Bioanal. Electrochem., Vol. 14, No. 4, 2022, 374-384

Analytical &
Bioanalytical
Electrochemistry

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Full Paper

Corrosion Inhibition of Carbon Steel in 1 M HCl using Monopolar Surfactants Derived From 3-Methyl-1,2,4-Triazole-5-Thione

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Received: 23 July 2021 / Received in revised form: 15 April 2022 /
Accepted: 18 April 2022/ Published online: 30 April 2022

Abstract- In this work, we have synthesized the surfactant compounds derived from 2-(N-Alkyl-3-methyl-1,2,4-triazolthioyl) acetic acid (MTSACCn; n=10, n=11 and n=12). These compounds have been purified and identified using several spectroscopic methods such as ^{1}H NMR; ^{13}C NMR spectroscopy. The molecular aggregation of MTSACCn has been foxed using tensiometer apparatus. The electrochemical study was carried out using a coupling of potentiodynamic and electrochemical impedance methods. The polarization curves indicate that the MTSACCn act as mixed-type inhibitors of carbon steel in 1M HCl solution. The electrochemical impedance spectroscopy measurements showed that all synthesized compounds act by establishing a barrier layer on the steel surface. Therefore, we noted that the inhibition efficiency increases with increasing of concentrations inhibitors. Also, the MTSACC12 is the best inhibitor, its inhibition efficiency reached a maximum value of 95% at 510^{-4} M. The adsorption of all surfactants studied follows the Langmuir isotherm.

Keywords- Surfactants; 1 M HCl solution; 1.2.4-triazole-5-thione; Inhibitor; Carbon steel

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1. INTRODUCTION

The surfactant molecules are widely used in several fields such as detergency, food, textile, pharmaceutical, and petroleum [1,2].

The surfactant molecules have been used as corrosion inhibitors by several authors [3-6]. These compounds have been shown to act at low concentrations by the establishment of an inhibitor film at the interface metal surface/corrosive solution. The inhibition efficiency of this kind of compound is better around a critical micelle concentration (CMC) [6].

In this work, we are interested in the synthesis of a triazole-thione polar head surfactant family MTSACCn and their use as corrosion inhibitors of carbon steel in 1M HCl.

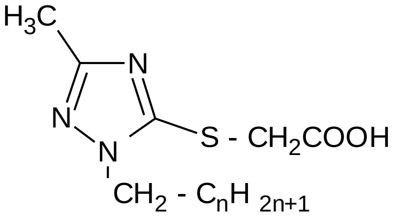
These molecules have been synthesized; purified in our laboratory and identified using usual spectroscopic methods such as ^{1}H NMR and ^{13}C NMR.

The electrochemical behavior of the carbon steel/1 M HCl interface has been studied by the stationary and transitory electrochemical methods completed by the surface analysis (SEM) in the presence and the absence of different concentrations of inhibitors.

2. EXPERIMENTAL SECTION

2.1. Inhibitor

Figure 1 shows the general structures of the isomeric compounds of MTSACCn surfactants used in this study. For MTSACC12 we have isolated only one isomeric compound.



n= 9,10,11

Figure 1. Structures of the synthesized inhibitor

2.2. Steel samples

The metal used is a cylindrical electrode made of carbon steel (E24), the surface area is 1cm². The chemical composition of the specimens other than iron according to the AFNOR standard are: % C: 0.2; % P: 0.005; % S: 0.05; % N: 0.07.

2.3. Attack solution

The 1M HCl medium has been prepared by diluting the 37% commercial HCl “Prolabo” with distilled water. All tests were carried out at room temperature in an aerated environment. Before each experimental test, the working electrode is polished with emery paper until the grade of 1200, degreased with acetone, and then dried at room temperature.

2.4. Electrochemical measurements

The electrochemical measurements were carried out by biologic Ptentiostat SP 200. the steel surface was the working electrode; a platinum one was used as the counter electrode and the saturated calomel electrode was used as the reference electrode (SCE). the electrode was maintained in the corrosive solution at free potential (OCP) for 30 minutes. Then the impedance diagrams and polarization curves were plotted respectively.

The polarization measurements were carried out scan rate of 1mV/s. The EIS measurements were made over a frequency domain from 100 KHz to 10 mHz. After the determination of the steady-state, the impedance diagrams are presented in the Nyquist plots.

2.5. Surface analysis

The SEM technique used in this study was conducted by Stereoscan 440 Lecia apparatus using the program LEO.

3. RESULTS AND DISCUSSION

3.1. Study of molecular aggregation in solution

The critical micelle concentration values of synthesized MTSACCn surfactants were determined from the break point of thesurface tension (mNm^{-1}) versus concentration (on log scale) curves (Figure 2).

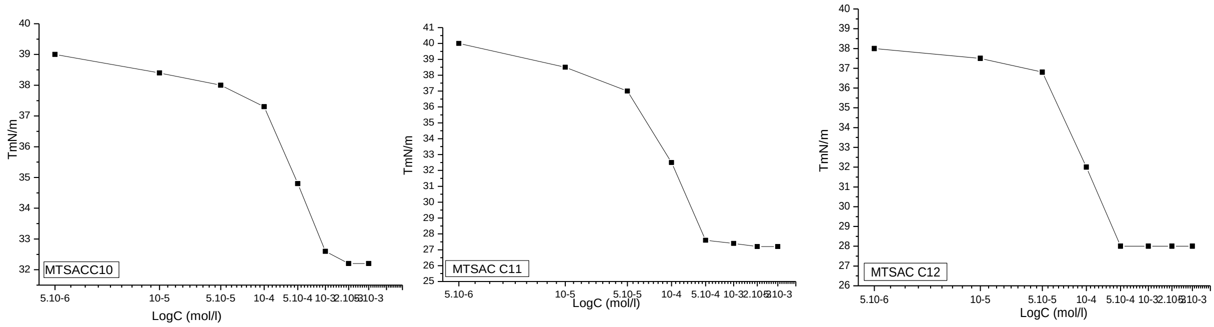


Figure 2. Surface tension versus log C of $MTSACC_{10}$, $MTSACC_{11}$ and $MTSACC_{12}$

Table 1. Aggregation parameters of investigated surfactants

Compounds	CMC (mol/l)	Tk (°C)
MTS AC C10	10^{-3}	<25
MTS AC C11	$5. 10^{-4}$	<25
MTS AC C12	2.10^{-4}	<25

The molecular aggregation parameters are shown in Table 1. We note that the CMC values decrease with increasing the alkyl chain length.

3.2. Effect of the concentration of inhibitors

3.2.1. Potentiodynamic studies

The polarization curves in the absence and the presence of MTSACC10, MTSACC11 and MTSACC12 at different concentrations in 1M HCl medium are shown in Figure 3.

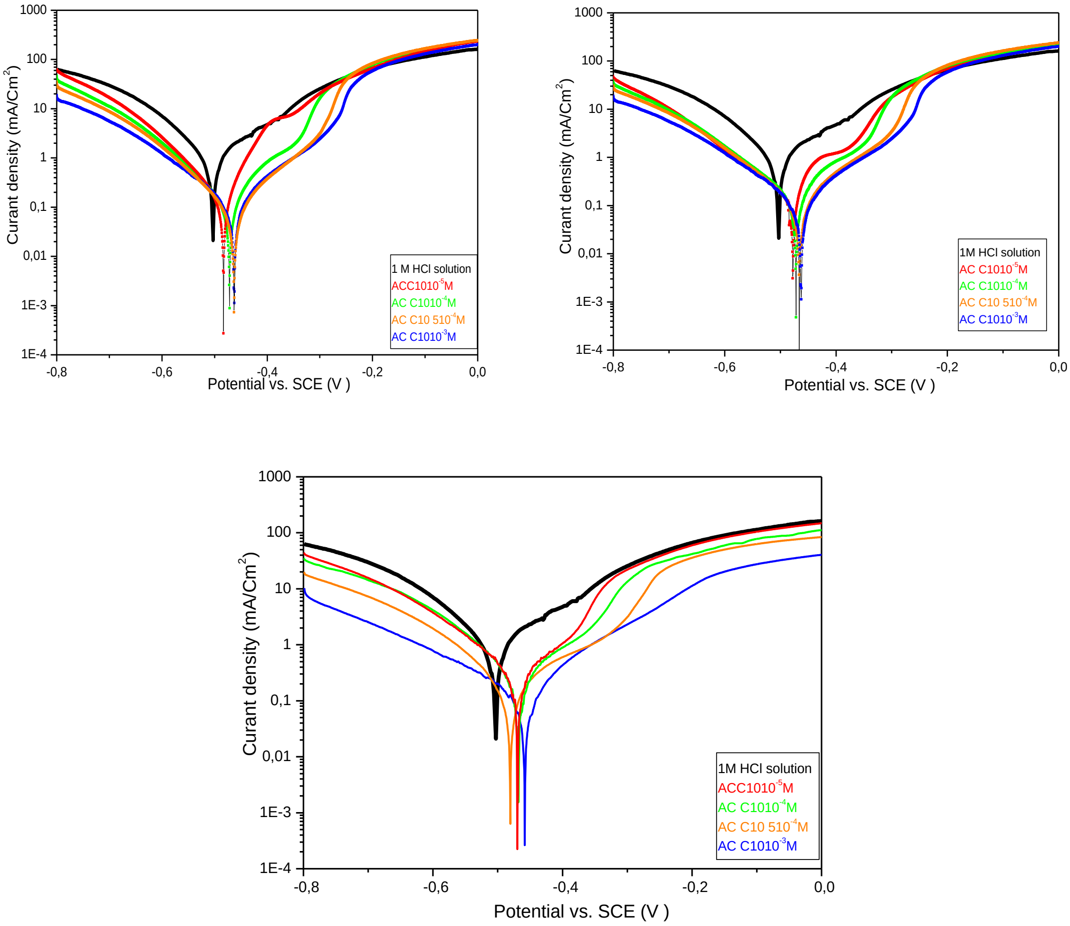


Figure 3. Potentiodynamic curves in the absence and the presence of different concentrations of MTSACC10; MTSACC11and MTSACC12

The polarization curves with inhibitors have the same electrochemical behavior, indeed, the shape of Tafel straight lines indicates that the reaction of reduction of hydrogen on the steel surface follows a pure activation mechanism.

The addition of these inhibitors leads to a decrease in the cathodic and the anodic current densities with a slight change in the corrosion potential. This shows that MTSACCn compounds act as mixed-type inhibitors.

The values of the electrochemical parameters for different concentrations of MTSAC C10; MTSAC C11 and MTSACC12 are reported in Table 2.

Table 2. Electrochemical parameters derived from the polarization curves

Inhibitors	Molar Concentrations	CMC	E_{corr} (mV)	I_{corr} (µA /Cm^2)	β_a (mV)	$-\beta_c$ (mV)	IE%
	0		- 487	393	86	98	-
MTSACC10	10^{-5}	10^{-3}	- 483	106	46	54	73
	10^{-4}		- 471	93	47	60	76
	5.10^{-4}		- 463	49	52	64	89
	10^{-3}		- 466	38	42	62	91
MTSACC11	10^{-5}	5.10^{-4}	- 480	67	52	100	80
	10^{-4}		- 471	45	42	55	87
	5.10^{-4}		- 466	28	50	56	92
	10^{-3}		- 464	27	49	64	92
MTSACC12	10^{-5}	2.10^{-4}	- 469	65	52	61	82
	10^{-4}		- 466	44	44	50	88
	5.10^{-4}		- 480	26	38	43	92
	10^{-3}		- 458	40	45	51	93

The corrosion inhibition efficiency (IE%) was defined as:

$$IE\% = \frac{I°_{corr} - I_{corr}}{I°_{corr}} X100 \qquad (1)$$

where I_{corr} and $I°_{corr}$ are the inhibited and uninhibited corrosion current densities respectively.

The analysis of the Table 2 shows that the inhibition efficiency (IE%) increases with increasing inhibitors concentrations and reaches a maximum value near the CMC.

The addition of these compounds is accompanied by a decrease of the cathodic and the anodic slopes, which shows that these compounds act with a change in the proton reduction reaction mechanism compared with the witness curve.

3.2.2. Electrochemical impedance measurements

The electrochemical impedance spectroscopy diagrams with and without various concentrations of the MTSACCn are shown in Figure 4.

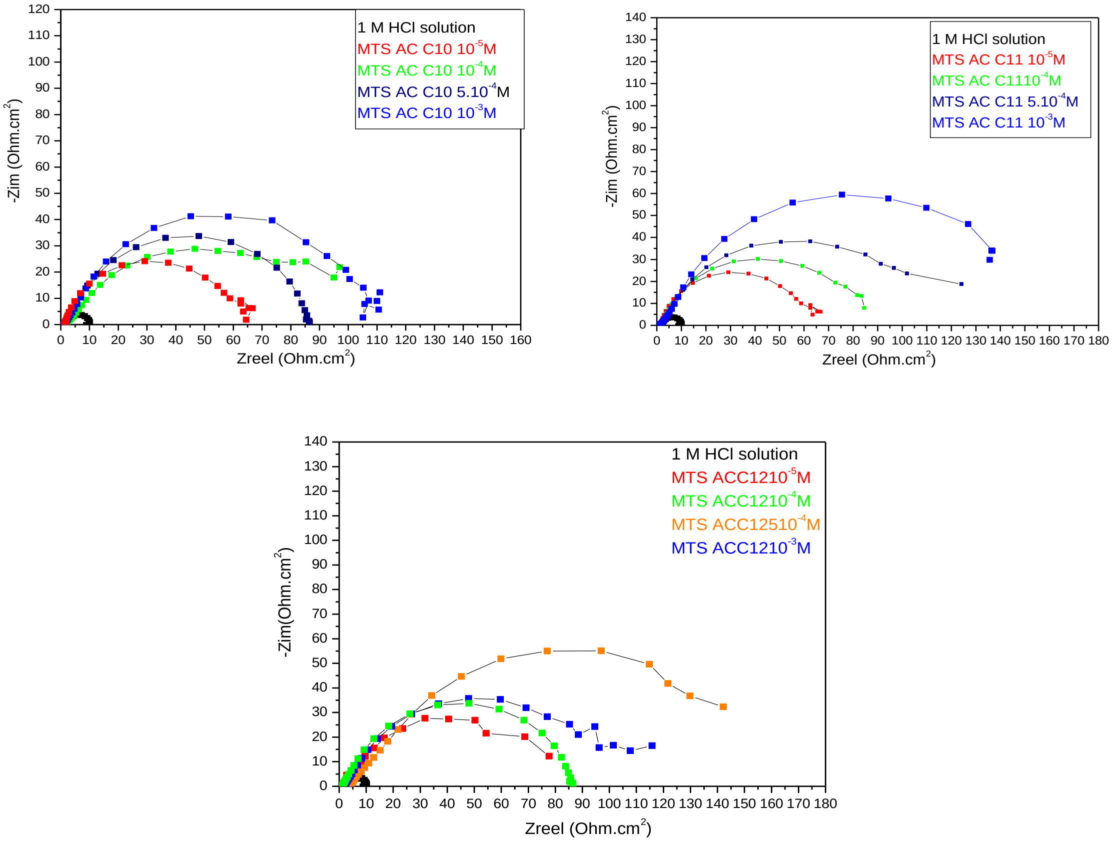


Figure 4. Electrochemical impedance diagrams without and with different concentrations of the MTSACCn (n=10,11,12) compounds

The analysis of Figure 4 shows the presence of the capacitive loops is not centered on the real axis. These phenomena often correspond to surface heterogeneity, which can be the result of the surface roughness, dislocations, the distribution of the sites, and active or adsorption of inhibitors [7].

In addition, the increase in the size of the capacitive loop with increasing the concentration of surfactants can be attributed to the charge transfer process. This result reflects the influence of the inhibitor on the process on the interface [8]. The modeling of the diagrams obtained by the EC-Lab software shows the appearance of a capacitive loop at high frequencies in the presence of inhibitors. With can be attributed to the formation of a film on the metal surface. The electrochemical parameters derived from impedance diagrams are shown in Table 3.

We note that the increase in the concentration of synthesized compounds leads to a significant increase in the values of charge transfer resistance (R_t), consequently, the inhibition efficiency increases and reaches a maximum value of 95% for the MTSACC12 at 5.10^{-4}M. This later has been selected as the best inhibitor.

Table 3. The electrochemical parameters issued from electrochemical impedance diagrams without and with various concentrations of the MTSACCn (n=10,11,12)

Inhibitors	**Concentrations (M)**	**CMC**	**R_e (ohm. cm^2)**	**R_f (ohm. cm^2)**	**C_f (µF./cm^2)**	**R_t (ohm .cm^2)**	**C_d (mF /cm^2)**	**IE %**
	0		**2.07**	------	--------	**8.2**	**2.63**	---
MTSACC10	10^{-5}	10^{-3}	1.18	0.414	90.00	65	1.44	86
	10^{-4}		1.04	0.37	19.74	90	1.38	90
	510^{-4}		0.84	0.53	0.98	88	1.33	91
	10^{-3}		0.97	0.48	0.98	114	0.96	93
MTSACC11	10^{-5}	5.10^{-4}	1.35	0.083	0.94	64.21	1.09	86
	10^{-4}		1.23	0.150	0.95	93	1.04	91
	510^{-4}		0.88	0.496	0.84	116	0.99	93
	10^{-3}		0.84	1.017	0.85	141	1.01	94
MTSACC12	10^{-5}	2.10^{-4}	2.22	0.041	1.65	76	1.12	88
	10^{-4}		1.36	2.41	1.04	88	1.95	91
	510^{-4}		2.49	1.44	0.89	156	1.04	95
	10^{-3}		0.82	0.62	2.92	108	1.08	93

Furthermore, the change in the values of R_t is due to a progressive replacement of the water molecules, by the cations of the surfactant adsorbed on the steel surface via the chloride anions, according to the results obtained by the authors [9].

In the presence of the MTSACCn, the double-layer capacitance (C_{dl}) decreases. Indeed, it passes from 2.63 mF to 1.0 mF in the presence of MTSACC12 at 5.10^{-4}M. This decrease is associated with the increase in the thickness of the organic layer formed by the inhibitor according to the expression given by the Helmholtz model [10-12]:

$$C_d = \frac{\varepsilon \varepsilon_0}{e} S \qquad (2)$$

where:

- e is the thickness of the deposit,
- S is the surface of the electrode,
- ε_0 is the permittivity of thevacuum
- ε is the dielectric constant.

The synthesized inhibitor is characterized by its positive quaternary ammonium charge, in a corrosive medium, which facilitates its adsorption on the negatively charged metal [11].

From these results, to describe the 1M HCl / steel interface, and to better analyze the resultsobtained using the EIS diagrams, the following electrical circuit was adopted (Figure 5).

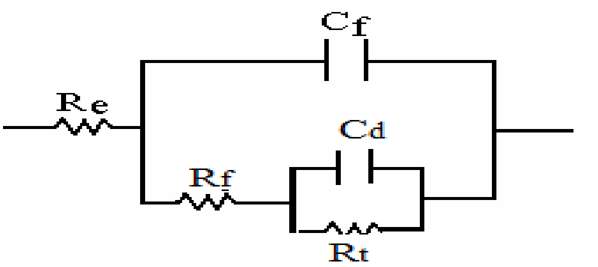


Figure 5. Scheme of the descriptive equivalent circuit

3.2.3. Absorption isotherm

The coverage surface values (θ) for different concentrations of the MTSACCn, from the results obtained by the polarization curves, were used to determine the corresponding isotherm to the adsorption process of the inhibitor.

The coverage surface (θ) can be determined by the following relationship:

$$\frac{C}{\theta} = \frac{1}{K} + C_{inh} \qquad (3)$$

The plot of the C_{inh} / ϴ curves as a function of the concentrations of the inhibitor is linear (Figure 6), indicating that the adsorption of the products tested is according to the model of the Langmuir isotherm.

The extrapolation of this curve to the y-intercept gives the value of K_{ads}. The standard free energy adsorption ΔG_{ads} was determined by the following equation:

$$\Delta G^{\circ}_{ads} = - RT \, Ln\,(55.5 * K_{ads}) \qquad (4)$$

- K_{ads}: the adsorption equilibrium constant
- ΔG^{o}_{ads} the free adsorption enthalpy
- R: the gas constant.
- T: the ambient temperature.
- θ: the surface coverage.
- 55.5 is the concentration of water in mol / l

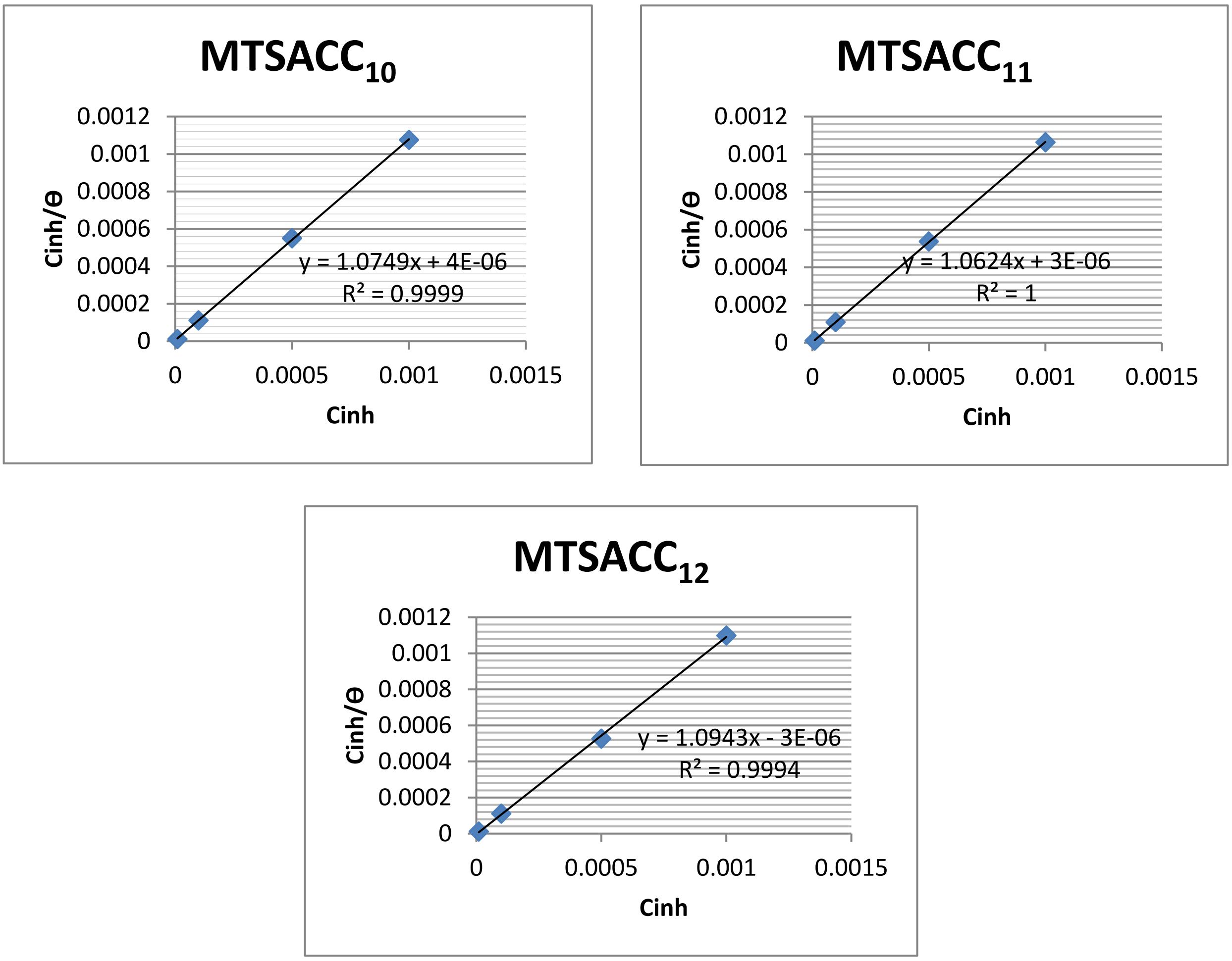


Figure 6. The plot (C/ϴ) as a function of the concentration for MTS ACC_{10}; MTS $ACC_{11}$and MTS ACC_{12}

The linear plots obtained in Figure 6 shows that the adsorption of surfactants inhibitors molecules on the metalsurface followed the Langmuir isotherm.

Table 4. Thermodynamic parameters of Langmuir adsorption

Inhibitors	**K_{ads} (mol^{-1})**	**Regression Coefficient (R^2)**	**ΔG_{ads} (Kj /mol)**
MTS AC C_{10}	250000	0.999	-40.77
MTS AC C_{11}	333333	1	-41.48
MTS AC C_{12}	5000000	0.999	-42.49

The obtained values of ΔGads are negative and are around -40 $kJ.mol^{-1}$, which leads that all the surfactants obey the chemisorption processes on the surface of the steel.

3.2.4. Surface analysis

In order to determine the morphology of the steel surface in the corrosive medium, The Scanning Electron Microscopy technique (SEM) observations were carried out on the steel samples in 1M HCl solution at room temperature in the absence and the presence of the MTSACC12 at a concentration of 5.10^{-4}M after 24 hours of immersion time (Figure 7a,b).

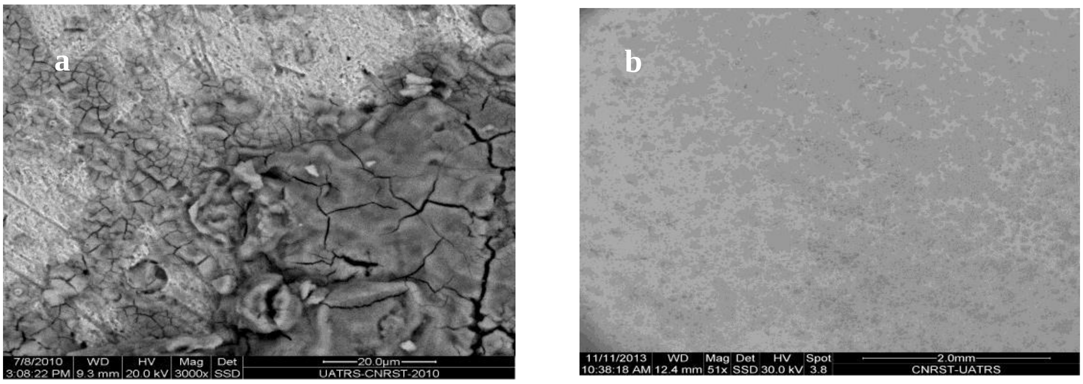


Figure 7. SEM micrography of the steel substrate after 24 hours immersion in 1M HCl solution without (a) and with 5.10^{-4}M MTS AC C12 (b)

The analysis of Figure 7 shows that the steel's micrography reveals in the absence of MTSACC12 several attacks due to metal corrosion. In the presence of this compound, the surface of the electrode remains intact. It's can be explained by the formation of an inhibitor film on the metal surface. These results were in concordance with those obtained by the electrochemical measurements.

4. CONCLUSION

According to the results obtained on the use of surfactants MTSACCn as corrosion inhibitors of carbon steel in HCl 1M, the following conclusions are drawn:

- The three surfactant compounds in the series of 2- (N-Alkyl-3-methyl-1,2,4-triazolthioyl) acetic acid (MTSAC C_{10}, MTSAC C_{11}, and MTSAC C_{12}) were synthesized in our laboratory, purified and characterized.
- The CMC values of MTSACn surfactants were determined by surface tension measurement.
- The potentiodynamic study showed that These surfactants reduce both cathodic and anodic corrosion current densities. It can be classified as a mixed types inhibitor.
- At the same inhibitor's concentration, the inhibition efficiency of MTSACn increases with the increasing length of the alkyl chain.
- The inhibition efficiency increases with the increase of concentration of the inhibitor and reached a maximum value of 95%, for MTSACC12 at 5.10^{-4} M.

- The adsorption processes of the three surfactants on the steel surface in the corrosive medium obeys the Langmuir isotherm which can be explained by the spontaneous reaction.

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