

# Synthesis of surfactants derived from 3-méthyl-1,2,4-triazole-5-thione and their inhibitive effect on carbon steel corrosion in hydrochloric acid medium

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**Abstract**— A series of new amphiphiles based on 3-methyl-1,2,4-triazole-5-thione have been synthesized and characterized by different spectral methods such as NMR and IR spectra. Their surface and self-aggregation properties in hydrochloric acid medium were evaluated. The critical micellar concentrations (CMC) decrease with increasing chain length. The synthesized compounds were tested as corrosion inhibitors for mild steel in 1M HCl solution using potentiodynamic polarization, impedance spectra and surface analysis. It has been observed that corrosion rate decreases, meaning an increase of efficiencies with increasing surfactants concentrations. Potentiodynamic polarization results revealed that the tested compounds act as mixed type inhibitors. The EIS measurements show that the inhibition effect is the results of formation an inhibitor film on the mild steel surface. This result was confirmed by the SEM techniques.

**Keywords** — Surfactants, CMC, Corrosion, Inhibition, Triazole-thione, mild steel, HCl,

## 1 INTRODUCTION

Mild steel has been widely used in many chemical industries due to its low cost and easy availability for fabrication of tanks and pipes etc. Mild steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions [1,2]. HCl is probably most corrosive solution in many industries particularly at elevated temperature environments. Almost all the industries are finds difficulties to control the corrosion. Acid inhibitors are usually used in several industrial processes to control the corrosion of metals. So selecting the appropriate inhibitor for particular metal is very important [3,4]. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms through which they get adsorbed on the metal surface [5-9]. The influence of organic compounds containing nitrogen such as amines and heterocyclic compounds on the corrosion of mild steel in acidic solutions has been investigated by several works [10-14]. Some studies have shown that the inhibition of the corrosion process is mainly decided by the formation of

donor-acceptor surface complexes between free or  $\pi$  electrons of an inhibitor and vacant d orbital of a metal [15-17]. The effect of inhibitors adsorbed on metallic surfaces in acid solutions is to slow of the metal. Such effect is obtained by forming a barrier of diffusion or by means of the blockage of the reaction sites and thereby reducing the corrosion rate [18]. The aim of this work is to evaluated the corrosion inhibition efficiency of some surfactants derived from triazolethione containing nitrogen, sulphur, oxygen and aromatic ring for mild steel in 1M HCl at 25°C using potentiodynamic polarization, EIS spectra and SEM techniques.

## 2 Experimental procedure

### 2.1 Sample

Mild steel specimens of composition Fe = 99.675, C = 0.2, P = 0.005, S = 0.05, N = 0.07 were cut to size of 1 cm X 1 cm. The surface of specimens were polished with emery papers ranging from 180 to 1200 grades and decreased with acetone, washed and dried.

### 2.2 Attack Solution

The electrolyte solution was 1 M HCl, which was prepared from the commercial "prolabo" reagent and double-distilled water.

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\*A.Srhiri, Servichim Society, SARL Production of corrosion Inhibitions.

### 2.3 Inhibitors

The organic compounds tested as corrosion inhibitors have been synthesized by grafting alkyl chains as hydrophobic tails on 3-methyl-1,2,4-triazole-5-thione moieties as hydrophilic heads. Followed by grafting the acetic acid using N-alkylation method. Structures of the synthesized compounds namely Acide-2(S-decyl1,2,4- triazolyl) acetique (MTSC10AC), Acide-2(S-Undecyl1,2,4- triazolyl) acetique (MTSC11AC) and Acide-2(S-Dodecyl1,2,4- triazolyl) acetique(MTSC12AC) were confirmed by 1H-NMR and 13C-NMR spectral analysis (Figure 1).

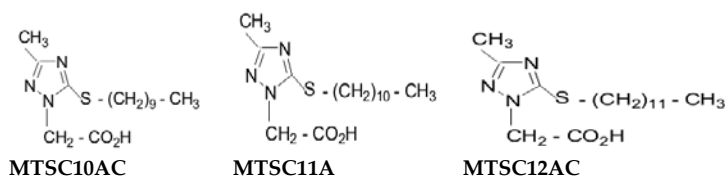


Figure 1: Molecular structures of inhibitors synthesized

### 2.4 Potentiostatic Polarisation studies

Electrochemical measurements were conducted in a conventional three-electrode cylindrical glass. A platinum disc was used as counter electrode and the Ag/AgCl as reference electrode. The working electrode was a carbon steel disc. The specimens were machined into cylinders and mounted in polytetra-fluoroethylene (PTFE) moulds. The area in contact with the corrosive solution was 1cm<sup>2</sup>. The potentiodynamic polarisation curves were recorded using a Biologic Potentiostat PS 200, at a scan rate of 0.5 mV/s. Before recording, the steel electrode was maintained at E<sub>corr</sub> for 30mn. Then the electrode was swept from cathodic potential to anodic potential.

### 2.5 Electrochemical impedance spectroscopy

The EIS measurements were carried out with an electrochemical potentiostat suitable for measuring small currents and high impedances (Biologic Potentiostat PS 200). At E<sub>corr</sub>, after immersion in solution without bubbling. A circular surface of the carbon steel of 1 cm<sup>2</sup> area was exposed to the solution. After the determination of the steady-state current at a given potential, sine wave voltage (10mV) peak-to-peak, at frequencies between 100 kHz and 10mHZ, were superimposed on the rest potential. The impedance diagrams then obtained are presented in the Nyquist representation.

### 2.6 Surface analysis (Scanning Electron Micrograph)

The surface morphology of the electrode was examined with a scanning electron microscope (Leica stereoxam 440). After 24 h of immersion with and without inhibitor, the specimens were cleaned with double distilled water and

dried at room temperature.

## 3 Results and discussions

### 3.1 Potentiodynamic measurements

Polarisation curves of the mild steel electrode in 1M HCl with and without various concentrations of surfactants studied at room temperature are shown in figure 2, 3 and 4.

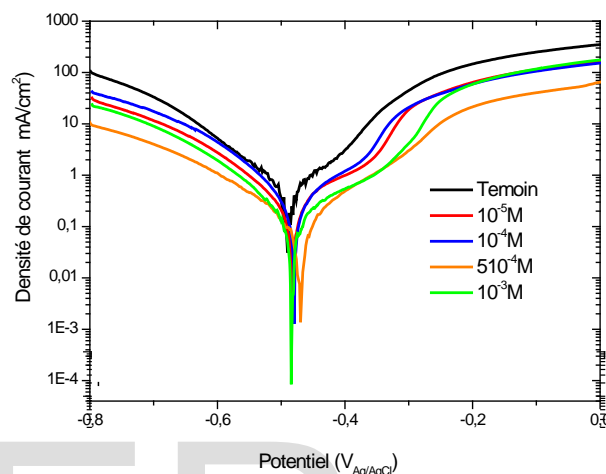


Fig 2: Polarization curves of steel in 1M HCl with and without MTSC<sub>10</sub>AC at different concentrations

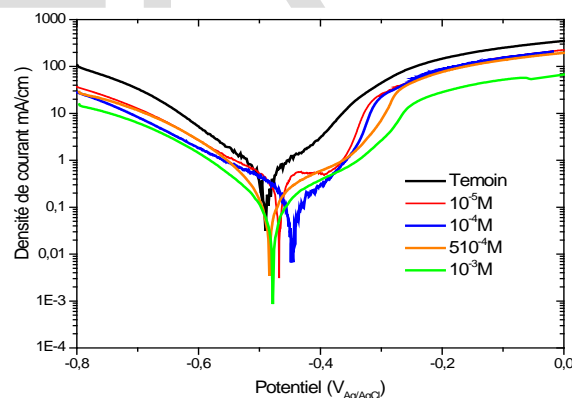
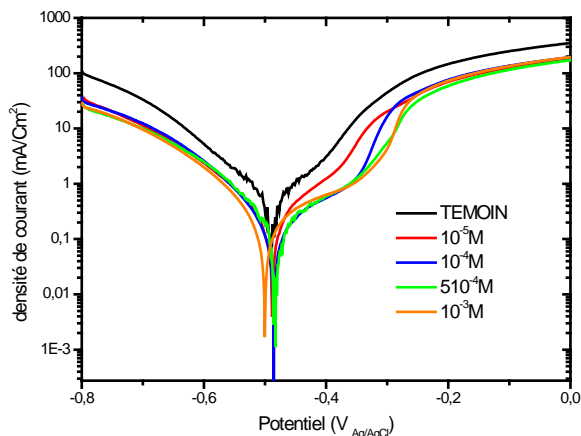


Fig 3: Polarization curves of steel in 1M HCl with and without MTSC<sub>11</sub>AC at different concentrations



**Fig 4:** Polarization curves of steel in 1M HCl with and without MTSC<sub>12</sub>AC at different concentrations

It shows that the addition of inhibitors to the acid solution shifts the cathodic and anodic current densities with a slight modification of corrosion potential when the concentration of inhibitors increases. These results revealed that the inhibitors act as mixed ones. Probably attributed to the adsorption of the inhibitor film on the steel surface. The lowest currents densities were obtained in the case of MTSC<sub>10</sub>AC.

Values of associated electrochemical parameters such as corrosion potential ( $E_{corr}$ ), cathodic Tafel slope ( $B_c$ ), corrosion current density ( $I_{corr}$ ) and inhibition efficiencies ( $E\%$ ) for all compounds tested are given in Table 1 (see below).

The values of corrosion current densities were obtained by extrapolation of cathodic and anodic Tafel lines to the respective free corrosion potential. The corrosion inhibition efficiency ( $E\%$ ) was defined as:

$$E\% = (1 - I_{corr}/I_{0corr}) \times 100 \quad (1)$$

Where  $I_{corr}$  and  $I_{0corr}$  are the inhibited and uninhibited corrosion current densities respectively.

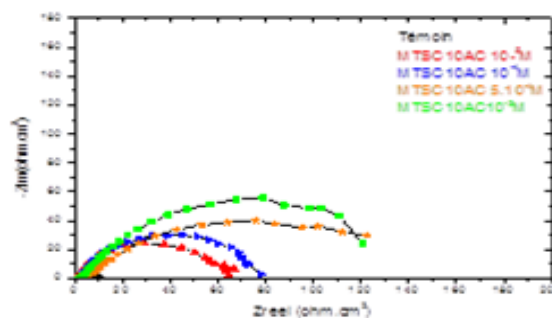
From the results obtained in Table 1, we note that:

- The corrosion current density ( $I_{corr}$ ) decrease with increasing the concentrations of the inhibitors.
- The efficiency increase with increasing inhibitor concentrations and reach a maximum around a CMC value. The maximum inhibition efficiency was found to be 93% for  $5.10^{-4}M$  of MTSC<sub>12</sub>AC.
- The slopes of the anodic and cathodic tafel lines were slightly changed on increasing the concentrations of inhibitors. This indicates that there is no change of the mechanism of the inhibition in presence and absence of inhibitors.

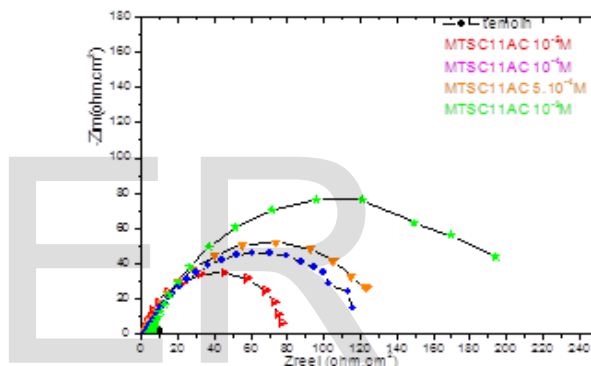
### 3.2 EIS measurements

EIS method was carried out to obtain more information

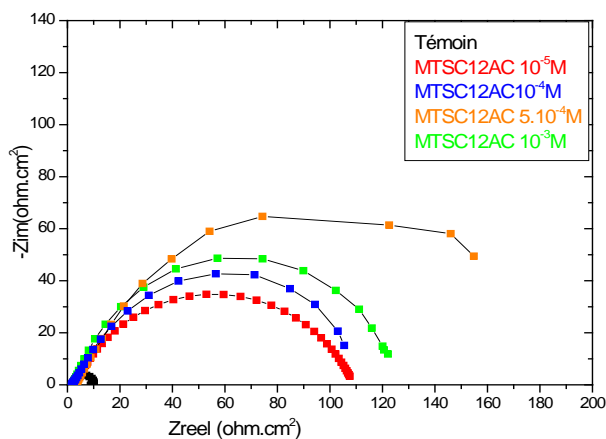
about the corrosion behaviour at the steel/acid interface. Figure 5, 6 and 7 shows the EIS curves of steel in 1M HCl in the presence and absence of MTSC<sub>n</sub>AC ( $n=10, 11, 12$ ).



**Fig 5:** Nyquist plots of steel in 1M HCl without and with MTSC<sub>10</sub>AC at different concentrations



**Fig 6 :** Nyquist plots of steel in 1M HCl without and with MTSC<sub>11</sub>AC at different concentrations



**Fig7:** Nyquist plots of steel in 1M HCl without and with MTSC<sub>12</sub>AC at different concentrations

In the absence of inhibitor, one capacitive loop is observed.

In the context of a detailed study published elsewhere [19], this loop is attributed to a charge transfer process.

In the presence of inhibitors, two capacitive loops were appeared. One at high frequencies with low capacity value attributed to an inhibitor film with adsorbed on the steel surface. The second loop at low frequencies was attributed to the charge transfer process. The  $R_t$  increase with increasing inhibitors concentrations.

Table 2 (see below) gives the values of the charge transfer resistance  $R_{ct}$ , double-layer capacitance  $C_{dl}$ , and inhibition efficiency obtained from the above plots.

containing MTSC10AC, MTSC11AC and MTSC12AC at different concentrations

The percent inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the equation:

$$IE \% = \frac{R_t^{-1} - R_{t(inh)}^{-1}}{R_t^{-1}} \times 100$$

Where  $R_{t(inh)}$  and  $R_t$  are the charge transfer resistance in the presence and absence of inhibitors.

We note that the  $R_t$  increase with increasing inhibitors concentrations. Consequently, the inhibition efficiency increase. The high efficiency values were obtained around corresponding CMC values. The MTSC12AC was selected as the best inhibitor. With confirm the results obtained by the potentiodynamic studies. A decrease in the  $C$  values, suggested that the MTSCnAC molecules act by adsorption at the metal-solution interface [20].

The results described above can be interpreted in terms of the equivalent circuit of the electrical double layer shown in fig. 8, which has been used previously to model the steel-acid interface.

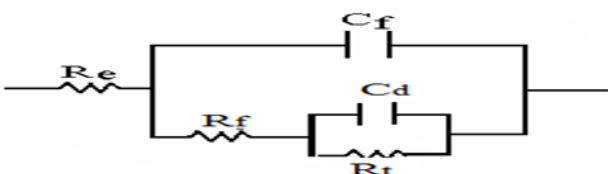


Fig. 8: Equivalent circuit model for studied inhibitors

- $R_e$  : solution resistance
- $R_t$  : charge-transfer resistance
- $C_f$  : Film capacitance
- $C_d$  : double layer capacitance.

### 3.3 Influence of immersion time

Figure 9 shows the impedance diagrams obtained in 1M HCl solution at  $10^{-3}M$  of MTSC12AC at the corrosion

potential after the carbon steel electrode was exposed to the solution for different times.

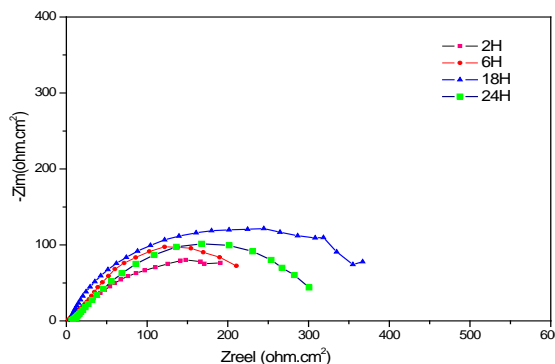


Fig 9: Complex plane plots of the impedance data obtained from the carbon steel electrode exposed for different times to the 1 M HCl solution with  $10^{-3}M$  MTSC12AC

It maintains the same shape after 30 min of immersion. The associated parameters are listed in Table 3.

Table 3: Electrochemical impedance parameters of the carbon steel in 1 M HCl solution with  $10^{-3}M$  of MTSC12AC for different immersion times.

Inhibitors	Temps	$R_e$ ( $\Omega.cm^2$ )	$R_f$ ( $\Omega.cm^2$ )	$C_f$ ( $\mu F/cm^2$ )	$R_t$ ( $\Omega.cm^2$ )	$C_d$ ( $mF/cm^2$ )
MTSC12AC	2H	2.96	2.45	11.20	266	0.76
	6H	5.33	1.49	11.92	297	0.71
	18H	4.05	0.12	2.18	424	0.14
	24H	7.23	2.69	6.36	356	0.83

The effect of increasing immersion time on impedance spectra is characterized by the increasing  $R_t$  value, reaching a maximum in 18 h. Consequently, the efficiency increases, and attained 93% at 18H.

### 3.4 Surface analysis (Scanning Electron Micrograph)

The micrographs of the mild steel surface in the presence of 1M HCl with and without MTSC12AC at  $10^{-3}M$  are shown in Figure 10. In the absence of inhibitor the surface was covered with a high density of pits. In the presence of the inhibitor the micrograph shows a few of pitting but shows a smooth surface. This result is due to the adsorption of inhibitor molecules on steel surface. This passive film blocks the active sites present on the metal surface [21].

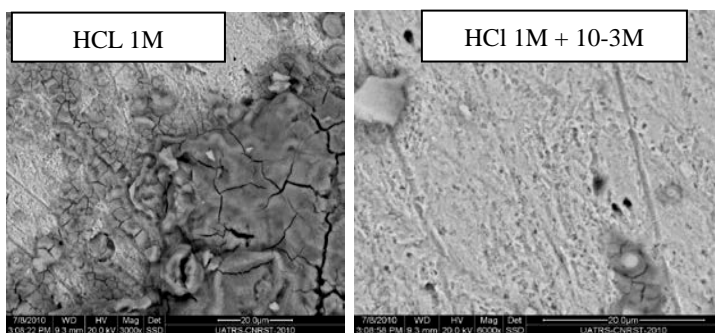


Fig 10: SEM micrographs of mild steel in 1M HCl with and without MTSC12AC

## 4 Conclusion

The following conclusions were made from the study:

-Inhibition efficiency of the newly synthesised Triazolethione derivatives was increased with increasing concentration of inhibitor. The maximum inhibition efficiency was found to be 91% in 1M HCl for  $10^{-3}$ M of MTSC12AC. At 25 °C.

-Shifts of cathodic and anodic current densities with a slight modification of corrosion potential when the concentration of inhibitors increases suggested that triazolethione derivatives behave as mixed type inhibitor.

-The Scanning Electron Micrograph technique shows that in the absence of inhibitor the surface was covered with a high density of pits. In the presence of the inhibitor the micrograph shows a few of pitting but shows a smooth surface. This result is due to the adsorption of inhibitor molecules on steel surface.

## REFERENCES

- [1] S. D. Shetty, P. Shetty, H. V. S. Nayak, J. Serb. Chem. Soc., 71 (10) (2006) 1073.
- [2] R. Touir, N. Dkhireche, M. Ebn Touhami, M. Sfaira, O. Senhaji, J.J. Robin, B. Boutevin, M. Cherkaoui, Mater. Chem. Phys., 122 (2010) 1–9.
- [3] H.P. Sachin, M.H. Moinuddin Khan, N.S. Bhujangaiah, Int. J. Electrochem. Sci., 4( 2009) 134-143
- [4] Libin Tang, Xueming Li, Yunsen Si, Guannan Mu, Guangheng Liu, Mater. Chem. Phys., 95(2006)29.
- [5] A.O.James, N.C. Oforika, O.K.Abiola and B.I.Ita,” A study on the inhibition of mild steel corrosion in HCl by pyridoxol hydrochloride”, Eclectica Quimico, Volume 32, No.3, 2007.
- [6] K.Parameswari, S.Rekha, S.Chitra, E.Kayalvizhy, Study on the Inhibition of Mild Steel Corrosion by Benzoisoxazole and Benzopyrazole derivatives in H<sub>2</sub>SO<sub>4</sub> Medium , Portugaliae Electrochemica Acta, 28(3),( 2010) 189-201.
- [7] Keera S T and Omar A M A, “Efficiency of four cationic corrosion inhibitors for steel, Mans Sci, Bull (A-Chem) 23(1): (1996) 12-21.
- [8] Gomma G K, Corrosion inhibition of steel by benzotriazole in sulphuric acid, Material Chem. Phys. , 55, (1998) 235-240.
- [9] Atulkumar, Corrosion Inhibition of Mild Steel in HCl by Sodium Lauryl Sulfate (SLS)’, E-Journal of Chemistry, 5.2(2008),275.
- [10] S.A.Umoren, U.M.Eduok and E.F.Oguzies, Corrosion Inhibition of Mild Steel in 1M H<sub>2</sub>SO<sub>4</sub> by Polyvinyl Pyrrolidone and Synergistic Iodide Additives, Portugaliae Electrochimica Acta, 26/6, (2008)533.
- [11] R.B. Rastoyi, M. M. Singh, K. Singh, M. Yadav, Organolic Dithiohydrazodicarbonamides as Corrosion inhibitors for mild-steel-dimethyl sulphoxide containing HCl, Portugaliae Electrochimica Acta, 22, (2005), 315-332.

- [12] ASTM G 31-72, Standard Practice for Laboratory Immersion Corrosion Testing of Metals, West Conshohocken, PA: ASTM (1990).
- [13] S Divakara Shetty, Prakash Shetty & H V Sudhaker Nayak,” Inhibi-tion of corrosion of mild steel in HCl by N-cyclohexyl-N’-phenyl thiourea”, Indian Journal of Chemical Technology, 12, (2005), 462-465.
- [14] S.Muralidharan, R.Chandrasekar and S V K Iyer, “Effect of piperi-dones on hydrogen permeation and corrosion inhibition of mild steel in acidic solution”, Proc. Indian Acad.Sci (Chem.Sci) 12,2 (2000), 127-136
- [15] Khamis, Corrosion, 46(1990) 476.
- [16] Forsal, M. Ebn Touhami, B. Mernari, J. El Hajri, M. Filali Baba, Portug. electrochim. Acta, (2010) 203-212
- [17] K. Parameswari, S. Rekha, S. Chitra, E. Kayalvizhy, Portug. elec-trochim. Acta, (2010) 189-201
- [18] J.L.Mora-Mendoza, J.G.Chacon-Nava,G.Zavala-Olivars, M.A.Gonzalez-Nunez and S.Turgoose,” Influence of Turbulent Flow on the Localized Corrosion Process of Mild Steel with Inhibited Aqueous Carbon Dioxide Systems”, Corros Eng. 58 (2002) 608.
- [19] D. Chebabe, N. Hajjaji and A. Shiri, in: Proceeding of the 8th European Symposium on Corrosion Inhibitors (8SEIC), Ann. Univ. Ferrara, N.S., V, Suppl. 10, 1995.
- [20] F. Bentiss, M. Traisnel, M. Lagrenée, J. Applied Electrochem., 31 (2001)41-48.
- [21] A V Shanbhag, R A Prabhu, G M Kulkarni, R G Kalkhambkar and T V Venkatesha, Indian Journal of Chemical Technology,” Inhibitory effects of some imines on the corrosion of mild steel in HCl solution”, Vol.14, November (2007), 584-591

**Table 1:** Electrochemical kinetic parameters obtained from potentiodynamic polarization technique for the corrosion of carbon steel in 1M HCl at different concentrations of investigated inhibitors at 25 °C.

Inhibiteurs	Concentrations(M)	E <sub>corr</sub> (mv)	I <sub>corr</sub> (μA)	β <sub>a</sub> (mv)	-β <sub>c</sub> (mv)	E%	CMC
	0	-487	393	86	98		
MTSC <sub>10</sub> AC	10 <sup>-5</sup>	-482	69	35	40	82	9.10 <sup>-4</sup>
	10 <sup>-4</sup>	-479	68	31	34	83	
	5.10 <sup>-4</sup>	-465	38	34	63	90	
	10 <sup>-3</sup>	-484	34	36	38	91	
MTSC <sub>11</sub> AC	10 <sup>-5</sup>	-466	87	23	25	78	6.10 <sup>-4</sup>
	10 <sup>-4</sup>	-444	47	38	40	88	
	5.10 <sup>-4</sup>	-485	36	33	25	90	
	10 <sup>-3</sup>		38	43	55	91	
MTSC <sub>12</sub> AC	10 <sup>-5</sup>	-487	82	46	54	79	3.10 <sup>-4</sup>
	10 <sup>-4</sup>	-485	34	30	28	91	
	5.10 <sup>-4</sup>	-484	29	29	18	93	
	10 <sup>-3</sup>	-440	35	28	35	91	

**Table 2:** Electrochemical parameters derived from the Nyquist plots and inhibition efficiencies values for mild steel in 1 M HCl containing MTSC10AC, MTSC11AC and MTSC12AC at different concentrations

Inhibiteurs	Concentrations	R <sub>e</sub> (ohm. cm <sup>2</sup> )	R <sub>f</sub> (ohm. cm <sup>2</sup> )	C <sub>f</sub> (μF/cm <sup>2</sup> )	R <sub>t</sub> (ohm. cm <sup>2</sup> )	C <sub>d</sub> (mF/cm <sup>2</sup> )	E%	
	0M	2.07	-----	-----	8.2	2.63	-----	
MTSC <sub>10</sub> AC	10 <sup>-5</sup>	2.2	0.94	69	68	1.28	86	9.10 <sup>-4</sup>
	10 <sup>-4</sup>	2.34	0.04	1	78	1.10	88	
	510 <sup>-4</sup>	3.3	1.54	13	141	0.82	93	
	10 <sup>-3</sup>	2.00	1.37	9	169	0.89	94	
MTSC <sub>11</sub> AC	10 <sup>-5</sup>	0.80	2.64	12	79	0.33	89	6.10 <sup>-4</sup>
	10 <sup>-4</sup>	1.46	0.98	27	131	0.24	93	
	510 <sup>-4</sup>	1.64	0.81	11	128	0.74	93	
	10 <sup>-3</sup>	3.82	0.73	3.4	200	0.63	96	
MTSC <sub>12</sub> AC	10 <sup>-5</sup>	3.90	2.74	20	110	0.88	91	3.10 <sup>-4</sup>
	10 <sup>-4</sup>	1.87	2.64	2.98	118	0.51	93	
	510 <sup>-4</sup>	9.20	0.54	7.31	190	0.55	96	
	10 <sup>-3</sup>	1.83	0.49	2.25	130	0.96	94	