Effect of some oxadiazoles derivatives on the corrosion of mild steel in hydrochloric acid solution

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ABSTRACT

The inhibition of the corrosion of mild steel in 1M HCl by 2,5-bis(n-methylphenyl)-1,3,4-oxadiazole (n-DTOX) has been investigated at 30^0C using electrochemical and weight loss measurements. The comparative study of oxadiazoles derivatives indicates that the corrosion inhibition of 2,5-bis(3-methylphenyl)-1,3,4-oxadiazole being the most efficient and 2,5-bis(2-methylphenyl)-1,3,4-oxadiazole the least. The associated activation corrosion and free adsorption energies have been determined.
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INTRODUCTION

The corrosion of mild steel is a fundamental academic and industrial concern that has received considerable attention[1-4]. The protective action of an inhibitor in metal corrosion is often associated with chemical or physical adsorption, involving a variation in the charge of adsorbed substance and a transfer of charge from one phase to the other. Special attention was paid to the electron density on the atom or the group responsible for adsorption. Most of the efficient acid inhibitors are organic compounds which mainly contain nitrogen; sulphur or oxygen atoms in their structure; owing to unshared electron pair those atoms represent centres for chemisorptions processes[5,6]. In the present paper we describe the influence of some oxadiazoles derivatives on corrosion of mild steel in 1M HCl using weightless, electrochemical polarization techniques and electrochemical impedance spectroscopy.

EXPERIMENTAL

Material preparation

Mild steel strips containing 0.09wt.% P, 0.38wt.% Si, 0.01wt.% Al, 0.05wt.% Mn, 0.21wt.% C, 0.05 wt.% S and balance iron were used for electrochemical and gravimetric studies. Mild steel specimens were mechanically polished on wet SiC paper(400, 600 and 1200), washed with double-distilled water, degreased ultrasonically in ethanol, and finally dried at room temperature before being immersed in the acid solution. The temperature was controlled at 30 ± 1^0C. The acid solutions used were made from Riedel-de Haen. Appropriate concentrations of acid were prepared by using double-distilled water. The concentration range of inhibitors employed was 10^{-5}-3.10^{-4}M in 1M HCl. Inhibitors was synthesised following the procedure reported previously[7]. Figure 1 shows the molecular

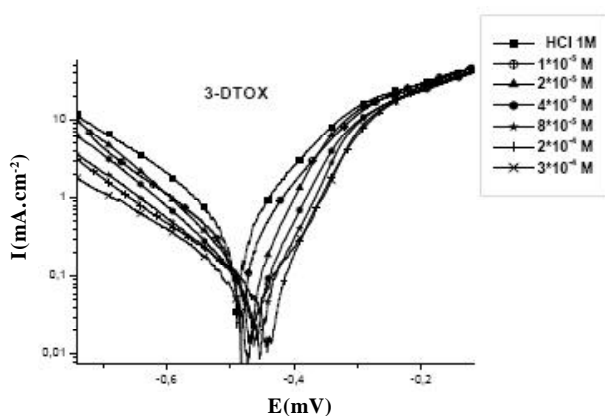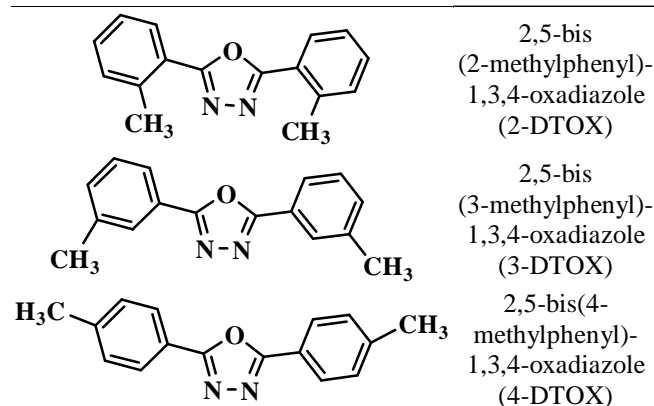**Figure 1: Molecular structure of oxadiazoles organic compounds studied**

	2,5-bis (2-methylphenyl)-1,3,4-oxadiazole (2-DTOX)
	2,5-bis (3-methylphenyl)-1,3,4-oxadiazole (3-DTOX)
	2,5-bis(4-methylphenyl)-1,3,4-oxadiazole (4-DTOX)

Figure 2: Polarization curves for mild steel in 1 M HCl containing different concentrations of 3-DTOX
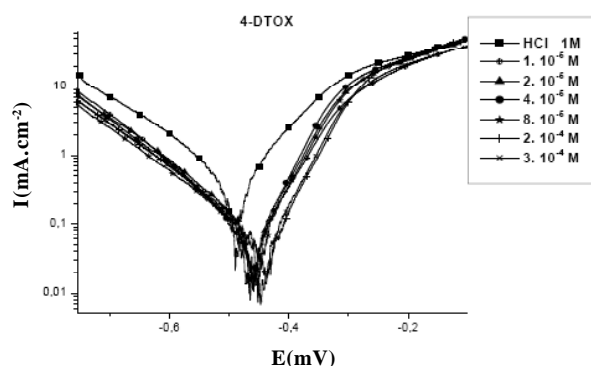

Figure 3: Polarization curves for mild steel in 1 M HCl containing different concentrations of 4-DTOX

structure of the investigated organic compounds, which have been labelled n-DTOX. When n=1, 2 or 3.

Electrochemical measurements

Electrochemical measurements were carried out by means of impedance equipment (Radiometer-analytical PGZ 100) and controlled with analysis software (Voltamaster 4).
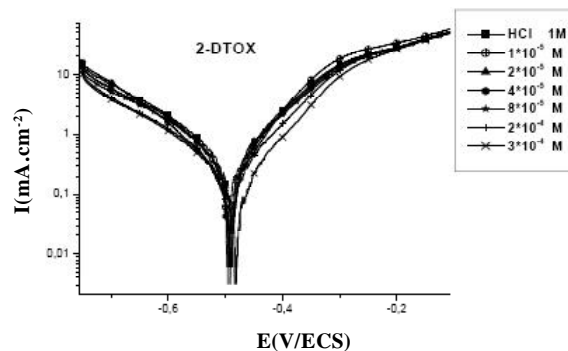

Figure 4: Polarization curves for mild steel in 1M HCl containing different concentrations of 2-DTOX

Potentiodynamic polarization curves-polarization experiments were carried out in a conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode(SCE) as reference. All tests were performed in continuously stirred conditions at room temperature. The procedure adopted for the polarization measurements was the same as described elsewhere[8]. For a given potential, the current was usually steady within 1h. The cathodic branch was always determined first; the open-circuit potential was then re-established and the anodic branch determined. The anodic and cathodic polarization curves were recorded by a constant sweep rate of $1mV.s^{-1}$. Inhibition efficiencies were determined from corrosion currents calculated by the Tafel extrapolation method and fitting the curve to the polarization equation.

$E\% = I - I'/I \times 100$

Electrochemical impedance spectroscopy(EIS)-Impedance spectra were obtained in the frequency range 100kHz-10mHz with 20 points per decade at the corrosion potential after 30min of immersion. A sine wave with 10mV amplitude was used to perturb the system. A SCE was used as reference and a Pt plate was used as counter electrode. All potentials are reported versus SCE. All tests were performed at 30^0C in non-de-aerated solutions under unstirred conditions.

The inhibition efficiency of corrosion of mild steel is calculated by charge transfer resistance as follows:

$E\% = Rec(inhib) - Rct/Rct(inhib) \times 100 = \theta \times 100$

where Rct and rec(inhib) are the charge transfer resistance values without and with inhibitor, respectively, for mild steel in 1M HCl.

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TABLE 1: Electrochemical parameters for the corrosion of mild steel in 1M HCl containing different concentrations of n-DTOX at 30⁰C and the corresponding corrosion efficiency

Product	Concentration M	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	$-\beta_c$ (mV/dec)	E (%)
blank	-	-490	326	132	-
	1.10^{-5}	-484	156	131	52
	2.10^{-5}	-471	88	123	73
	4.10^{-5}	-468	83	124	74
3-DTOX	8.10^{-5}	-461	76	119	76
	2.10^{-4}	-452	46	108	86
	3.10^{-4}	-440	39	104	88
	1.10^{-5}	-472	165	136	49
	2.10^{-5}	-465	95	150	70
	4.10^{-5}	-455	91	152	72
4-DTOX	8.10^{-5}	-458	77	159	76
	2.10^{-4}	-438	72	164	77
	3.10^{-4}	-445	70	156	78
	1.10^{-5}	-495	341	133	-4
	2.10^{-5}	-494	292	124	10
	4.10^{-5}	-487	283	124	13
2-DTOX	8.10^{-5}	-183	273	122	15
	2.10^{-4}	-480	262	123	19
	3.10^{-4}	-477	249	120	23

From TABLES 1 it can be concluded that: addition of n-DTOX does not change the value of E_{corr}; E(%) increases with inhibitor concentration, reaching the values 88, 78 and 23% at 3×10^{-4}M of 3-DTOX, 4-DTOX and 2-DTOX, respectively; the corrosion inhibition ability of the compounds listed is greater for 3-DTOX than for 4-DTOX and 2-DTOX.

TABLE 2: Impedance measurements and inhibition efficiency for mild steel in 1M HCl containing different concentrations of n-DTOX at 30⁰C

Product	Concentration M	R_{ct} ($\Omega.cm^2$)	C_d ($\mu F.cm^{-2}$)	E(%)
blanc	-	45.6	147	-
	1.10^{-5}	185.5	86.4	75.4
	2.10^{-5}	225	71.3	80
	4.10^{-5}	234	42.7	80.5
3-DTOX	8.10^{-5}	302	16.3	85
	2.10^{-4}	310	13.7	85.5
	3.10^{-4}	341.5	13	87
	1.10^{-5}	61	122	25
	2.10^{-5}	64	117	29
	4.10^{-5}	75	61.2	40
4-DTOX	8.10^{-5}	78	58.5	43
	2.10^{-4}	92	42	51
	3.10^{-4}	112	36	60
	1.10^{-5}	42.6	176	-7
	2.10^{-5}	44	164	-3
	4.10^{-5}	48.8	86	6.5
2-DTOX	8.10^{-5}	49.7	58	8.2
	2.10^{-4}	51	52	10.5
	3.10^{-4}	58	50	21.3

Weight loss measurements

Gravimetric experiments were carried out in a double-walled glass cell. The solution volume was 100cm³; the temperature of 30⁰C was controlled thermostatically. The weight loss of mild steel in 1 M HCl with and without the addition of inhibitor was determined after immersion in acid for 24 h. The mild steel specimens were rectangular in the form (1cm×4cm×0.06cm).

RESULTS AND DISCUSSION

Polarization curves

Anodic and cathodic polarization curves for mild steel in 1M HCl with various concentrations of n-DTOX are shown in figures 2, 3 and 4, respectively.

A decrease in both cathodic and anodic currents is noted. The cathodic current-potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the oxadiazoles studied does not modify the mechanism of this process[10]. The values of the corrosion potentials (TABLE 1) were not modified by addition of oxadiazole.

For anodic polarization in the presence of 1 M HCl (Figure 2), a voltage higher than -200 mV shows little effect on the presence of oxadiazoles when the potential became more positive than the desorption potential (E_d), or -200mV (Figure 2). This means that the inhibition mode of n-DTOX was dependent on the electrode potential. This is probably due to the increase in surface area as mild steel dissolves and organic compound desorbed. The behaviour of the oxadiazoles at potentials higher than -200mV may be the result of significant dissolution of the steel surface, leading to desorption of the adsorbed oxadiazole inhibitor from the electrode surface. In this case, the desorption rate of the oxadiazole is higher than its adsorption rate. However, the oxadiazole influence the anodic reaction at potentials more negative than -200mV. This indicates that n-DTOX exhibit both cathodic and anodic inhibition effects[11]. This observation is indication of mixed type control, n-DTOX mainly act as mixed type inhibitors in 1M HCl.

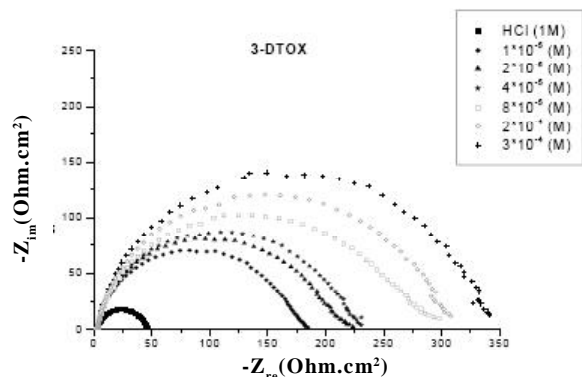Therefore, n-DTOX alone classified as an inhibitors

Figure 5: Nyquist diagrams for mild steel in 1M HCl containing different concentrations of 3-DTOX
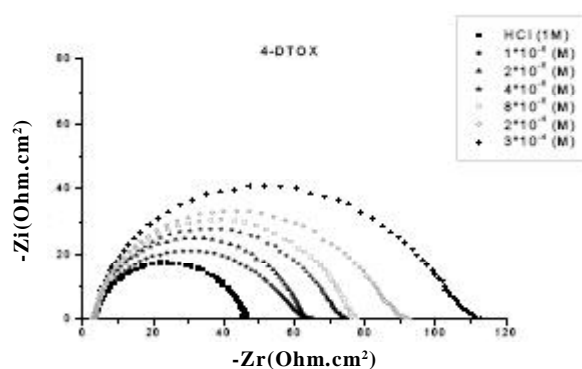

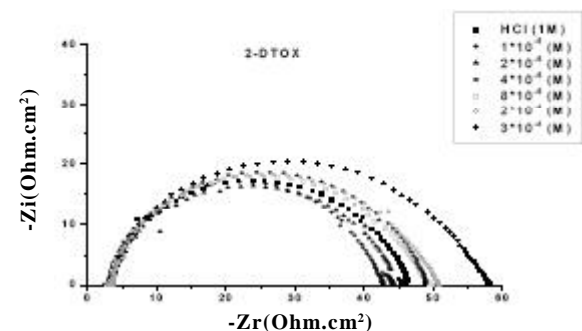**Figure 6: Nyquist diagrams for mild steel in 1M HCl containing different concentrations of 4-DTOX**

Figure 7: Nyquist diagrams for mild steel in 1M HCl containing different concentrations of 2-DTOX

of mixed type (anodic/cathodic inhibition).

EIS

The corrosion of mild steel in acidic solution in the presence of n-DTOX was investigated by the EIS method at 30⁰C after 30min immersion. The locus of the Nyquist plots was regarded as one part of a semicircle. Nyquist diagrams of mild steel in the presence and absence of inhibitors are shown in figures 5, 6 and

7. The values of charge-transfer resistance(R_t) and double layer capacitance(C_{dl}) were obtained from impedance measurements as described elsewhere[12]. The impedance parameters and values of E(%) are given in TABLE 2.

As the n-DTOX concentrations increased, the R_{ct} values increased, but the C_{dl} values tended to decrease. The decrease in C_{dl} values is due to the adsorption of n-DTOX on the metal surface[13].

The results obtained show that the inhibiting action of 3-DTOX is more pronounced than that of 4-DTOX and 2-DTOX. E(%) of 3-DTOX attains a value of 87% at 3×10^{-4} M for inhibitor in 1 M HCl.

The EIS study establishes the plot of C_{dl} versus concentration of n-DTOX. The shape of these curves is the same, so it can be concluded that an increase in the concentration of inhibitor leads to a decrease in the double layer capacitance up to a concentration of 3×10^{-4} M, were it remains almost constant. On the other hand, the inhibition efficiency values determined by EIS are smaller than those determined using the polarization curves. This difference is probably due to the shorter immersion time in the case of the polarization measurements.

As known, some atoms, such as O and N atoms of organic compound, which have unoccupied orbitals, so exhibit a tendency to obtain electrons. The electrons in the d-orbitals can easily be offered because their applied force is small. If an inhibitor does not only offer electrons to un occupied d orbitals of metals, but it can also accept of electrons in d-orbitals of metallic steel by using their antibond orbital to form stable chelate, then it may be considered an as excellent inhibitor[14]. The presence the electron donating groups on the organic compound structure (such CH_3) increases the electron density on the nitrogen of the C or N group, resulting high inhibition efficiency. Among the compounds investigated in the present study, C has been found to give the best performance as corrosion inhibitor.

Weight loss measurements

The values of inhibition efficiency and corrosion rate obtained from weight loss method at 3×10^{-4}M for inhibitor in 1M HCl at 30⁰C are summarized in TABLE 3.

The inhibition efficiency follows the order: 3-DTOX>4-DTOX2-DTOX.

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TABLE 3: Inhibition efficiency of 2-DTOX, 3-DTOX and 4-DTOX for the corrosion of mild steel in 1M HCl obtained from weight loss measurements at 30°C

Inhibitor	Inhibition efficiency %
3-DTOX	93.4
4-DTOX	70
2-DTOX	35.4

TABLE 4 : The influence of temperature on the electro chemical parameters for mild steel electrode immersed in 1 M HCl and in 1 M HCl+3×10⁻⁵M of 3-DTOX

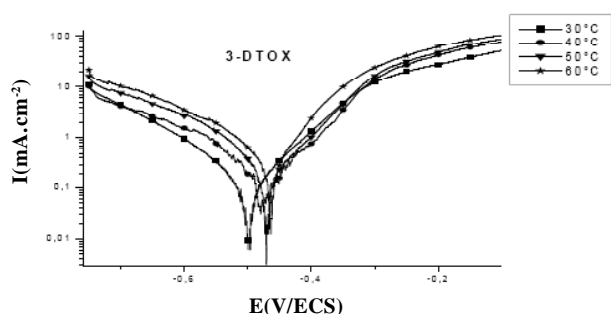| Temperature (°C)	Concentration (ppm)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	E(%)
30	Blank	-490	326	88
	80	-498	39	
40	Blank	-477.3	740	85
	80	-476.7	110	
50	Blank	-454.3	2144	85
	80	-470	321	
60	Blank	-475	3205	84
	80	-466	496	

Figure 8: Effect of temperature on the cathodic and anodic responses for mild steel in de-aerated 1M HCl + 3×10⁻⁵M of 3-DTOX
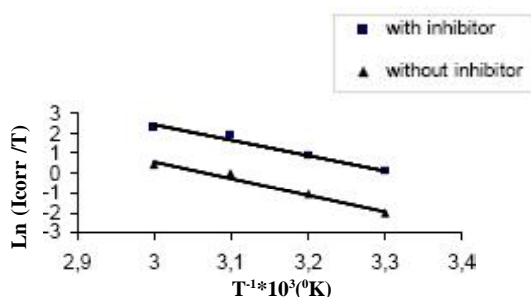

Figure 9: Arrhenius slopes calculated from corrosion current density for mild steel in: (A) 1M HCl and (B) 1M HCl + 3×10⁻⁵M of 3-DTOX

Effect of temperature

The temperature can modify the interaction between the mild steel electrode and the acidic medium in the absence and the presence of the inhibitor. Polarization curves for mild steel in 1M HCl without and with 3×

10^{-4} M of 3-DTOX in the temperature range 30-60⁰C are shown in figure 8.

Corresponding data are given in TABLE 4. In the studies temperature range, the corrosion current density increases with increasing temperature both in uninhibited and inhibited solutions and the values of the efficiency of 3-DTOX are nearly constant in the studied temperature range. The corrosion current density of steel increase more rapidly with temperature in the absence of the inhibitor. These results confirm that 3-DTOX acts as an efficient inhibitor in the range of temperature studied[15].

The corrosion reaction can be regarded as an Arrhenius-type process, the rate is given by[16,17]:

$$I_{corr} = Ke^{\frac{-E\alpha}{R}}$$

where k is the Arrhenius pre-exponential constant and E_a is the activation corrosion energy for the corrosion process.

Figure 9 Presents the Arrhenius plots of the logarithm of the corrosion current density versus 1/T, for 1M HCl, without and with addition of 3-DTOX. The values of the activation corrosion energy in the absence and presence of 3×10^{-4} M 3-DTOX were determined from the slopes of these plots and are calculated to be E_a = 69.72 kJ mol⁻¹ and 63.23kJ mol⁻¹. The reduction of the activation energy in the presence of 3-DTOX may be attributed to the chemisorption of molecules of this inhibitor on the mild steel[18,19]. The corrosion process corresponds to a different mechanism of the mild steel in presence of the inhibitor[20,21].

Adsorption isotherm

The adsorption of the inhibitor is influenced by the nature and the charge of the metal, the chemical structure of the inhibitor, distribution of the charge in the molecule, and the type of electrolyte[22,23]. Important information about the interaction between the inhibitor and steel surface can be provided by the adsorption isotherm. In the above work, it could be concluded that θ increases with the inhibitor concentration; this is attributed to more adsorption of inhibitor molecules onto the steel surface. As it is known, the adsorption of inhibitor is always a displacement reaction involving removal of absorbed water molecules from the metal surface[24]:

Org(sol) + nH₂O(ads)⇔Org(ads)+nH₂O(sol)

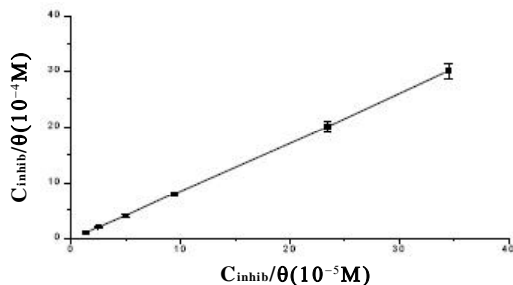Where Org (sol) and Org (ads) are the organic molecules in the

Figure 10: Langmuir isotherm adsorption model on the steel surface of 3-DTOX in 1M HCl
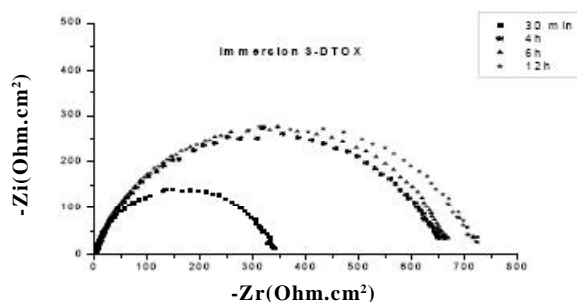

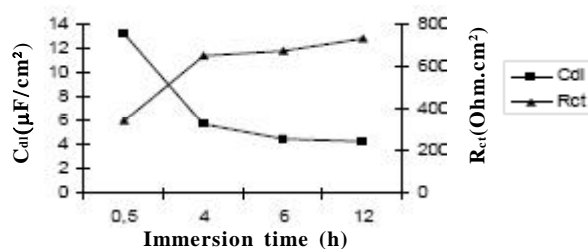**Figure 11: EIS spectra for mild steel in: 1 M HCl+3×10⁻⁵ M of 3-DTOX after various immersion at 30°C**

Figure 12: Variation of R_{ct} and C_{dl} with the immersion time for mild steel in: 1M HCl + 3×10⁻⁵ M of 3-DTOX after various immersion at 30°C

aqueous solution and adsorbed on the steel surface, respectively. H_2O (ads) is the water molecule on the steel surface; n is the size ratio representing the number of water molecules replaced by one unit of 3-DTOX.

Now, assuming that the adsorption of 3-DTOX belonged to the monolayer adsorption, then the Langmuir adsorption isotherm is applied to investigate the mechanism by the corrected equation[25]:

$$\frac{C_{inhib}}{\theta} = \eta C_{inhib} + \frac{n}{K_{ads}}$$

where n=1.14 and Kads is the adsorption coefficient.

The free energy of adsorption (ΔE_{ads}) values of 3-DTOX have been obtained by using the following equation[15]:

$$\Delta E_{ads} = - R.T.LnK_{ads}$$

resulted in -32.58KJ.mol⁻¹ for the experimental condition of this paper (Figure 10). This value indicates that the interaction between 3-DTOX and the surface of mild steel occurs by chemisorption[26].

Influence of the immersion time of 3-DTOX

Figure 11 presents the effect of the immersion time on the impedance spectra at the corrosion potential. The inhibitor concentration was set at 310⁻⁵M. The shape of these curves is very similar to that obtained when varying the inhibitor concentration.

The capacitive loop was found to increase in size with increase in immersion time, since more succinate anions will be electrostatically adsorbed on the positively charged steel surface. More details are shown in figure 12, which represents the variation of R_{ct} and C_{dl} with immersion time.

It is clear that the R_{ct} values increase sharply from 341 to 728 Ohm.cm² during the initial 12h and remained fairly constant afterward. At the same time, the capacitance values were reduced drastically from 13 to 4μF cm⁻² after 12h. These results demonstrate that the formation of the inhibitor surface film, and therefore the inhibitor adsorption, on the electrode surface was relatively fast and completed within 12h[27].

CONCLUSIONS

Concluding the experimental part, it was clearly demonstrated that all techniques used, especially electrochemical techniques are able to characterize and follow the inhibition of corrosion process promoted by the n-DTOX molecules. It was shown that the E(%) increase in the following order: 3-DTOX>4-DTOX>2-DTOX. The electrochemical impedance diagrams showed mainly a capacitive loop, which can be attributed to the formation of an adsorbed layer on the steel surface. The thermodynamic parameters indicated that 3-DTOX is chemisorbed on the metal surface and it's adsorption obeys to the modified Langmuir adsorption isotherm.

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