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Synthesis and Anticorrosion for Carbon Steel Of 4-Amino-3,5 Bis (4-Hydroxy-3-Methoxy)-1,2,4-Triazole in Hydrochloric Acid Solution.

H. El Attari[1], A. El Bribri[2], L. Mhaidra[1], F. Bentiss[3] and M. Siniti[4]
[1]*Laboratoire de Chimie de Coordination et d'Analytique, Faculté des Sciences, Université Chouaib Doukkali, El Jadida, Maroc*
[2]*Laboatoire de Chimie Organique et Bioorganique, Faculté des Sciences, Université Chouaib Doukkali, Maroc*
[3]*Laboratoire de Catalyse et Corrosion des Matériaux, Faculté des Sciences, Université Chouaib Doukkali, El Jadida, Maroc*
[4]*Equipe de Thermodynamique, Surfaces ,et Catalyse, Faculté des Sciences, Université Chouaib Doukkali, Maroc*

ABSTRACT : *4-amino -3,5bis (4-hydroxy-3-methoxy)-1,2,4-triazole (4-ABHMPT) was synthesized for the first time in the laboratory and his influence on the inhibition of corrosion of mild steel in 1N HCI was investigated by weight-loss and electrochemical impedance spectroscopy. The inhibition efficiency of this compound was found to vary with concentration and temperature . It is found that 4-ABHMPT is good inhibitor for corrosion of mild steel in 1N HCl. The maximum efficiency is about 98% for 4-ABHMPT at 300 mg.l*$^{-1}$ *concentration. The adsorption of this compound on the steel surface for both acids was found to obey Lagmuir's adsorption isotherm. The values of activation energy and free energy of adsorption indicated chimisorption on mild steel surface.*

KEYWORD(S): *triazole, mild Steel, Corrosion inhibitors, HCl*

I. INTRODUCTION

Acid solutions are widely used for the removal of rust, scale and corrosion products. The corrosion of steel in acid solutions and its inhibition constitute a complex problem of process. Generally, employing organic inhibitors to protect metallic components in these hostile environments is highly cost-effective **[1-6]**. Most of the test inhibitors are organic compounds containing sulfur or nitrogen in their chemical structures. It was found that this kind of compounds is chemically adsorbed on the metal surface forming a barrier for mass and charge transfer and consequently decreasing the rate of corrosion **[7-17]**. Triazole compounds are of interest as corrosion inhibitors for steel in acidic media **[18-25]**. The present work includes the synthesis and the study of corrosion behaviour of mild steel in 1 N HCl solution and its control by using a new triazole : 4-amino-3,5 bis (4-hydroxy-3-methoxy)-1,2,4-triazole. The inhibitive efficiencies of various inhibitors were determined by weight loss and electrochemical impedance spectroscopy. The nature of the inhibitor adsorption process was also studied and discussed.

II. EXPERIMENTAL DETAIL

Characteristic of the molecule :4-amino-3,5bis(4-hydroxy-3-methoxy)-1,2,4-triazole (4-ABHMPT) was synthesized in our laboratory following the procedure reported in the literature**[26]** and characterized by its spectral data. It was well dissolved in aqueous hydrochloric acid solutions. The structure formula of this compound is given in Figure 1:

Figure.1: 4-amino-3,5 bis (4-hydroxy-3-methoxy)-1,2,4-triazole (4-ABHMPT)

Yield = 63%, m.p. = 266°C
^{1}H NMR (DMSO): 4,10 ppm (s,6H); 6,1 ppm (s,2H); 7,1 ppm (d ,2H); 7,7 ppm (d, 2H); 7,8 ppm (s ,2H); 9,7 ppm (s,2H).
^{13}C NMR (DMSO): 133 ppm, 116 ppm , 119 ppm , 122 ppm , 148 ppm , 148 ppm , 154 ppm .
IR(Kbr): 3400, 3350-3000 bande large: 1700; 1600; 1550; 1500; 1400; 1300.

The elementary analysis of the element is given in Table 1.

Table.1: Elementary analysis of the element

% C $_{cal}$	%C $_{found}$	% H $_{cal}$	%H $_{found}$	% N $_{cal}$	% N $_{fond}$
58.54	58,50	4.88	4.79	17,17	17,17

Carbon steel samples with the following composition: 0.18 per cent (C), 0.02 per cent (Si), 0.47 per cent (Mn), 0.01 per cent (P), 0.02 per cent (S) and the remainder iron, were used in the studies. The samples were polished with emery papers from grade 120 to 1200, washed with distilled water, degreased with ethanol and dried at room temperature prior to each experiment.In weight loss experiments, the cleaned rectangular carbon steel specimens of size 50×20×0.6 mm were weighed before and after immersion in 1M HCl for 24 hours at 25°C in the absence and presence of the inhibitor. The weight loss was determined in mg.l^{-1}.hr^{-1}.

Solution of 1 N HCl was prepared from an analytical reagent grade 37% HCl and bidistilled water and was used as corrosion media.

Impedance measurements : Electrochemical impedance spectroscopy tests were conducted using an electrochemical measurement system (Tacussel) which comprised a digital potentiostat model Z computer. The impedance measurements were performed at the free corrosion potential (E_{corr}) over a frequency range of 100 kHz to 10 mHz, with a signal amplitude perturbation of 10 mV. Nyquist plots were obtained from the results of these experiments. Values of the charge transfer resistance (R_t) were obtained from these plots by determining the difference in the values of impedance at low and high frequencies, as suggested by Tsuru et al. **[27]**. Values of the double-layer capacitance C_{dl} were calculated from the frequency at which the impedance imaginary component $-Z_i$ was maximum. The Inhibition efficiencies $IE\%$ per cent were calculated using the following equation:

$$IE(\%) = \left(\frac{R_0^{-1} - R_t^{-1}}{R_0^{-1}} \right) \qquad (1)$$

Where R$_t$ and R$_0$ are the charge transfer resistance values without and with inhibitor, respectively.

The percentage inhibition (IE %) of mild steel was determined from weight loss as follows:

$$IE = \left(\frac{w_0 - w}{w_0} \right) \times 100 \qquad (2)$$

where w_0 and w are the corrosion rate of steel due to the dissolution in 1M HCl in the absence and the presence of definite concentrations of inhibitor, respectively.

III. RESULTS AND DISCUSSION

Weight loss measurements

Table 2 gives the values of percentage inhibition efficiency and corrosion rate obtained by weight-loss method with addition of different concentrations of 4-ABHMPT for 24 h of immersion time in 1N HCl at room temperature (25°C).

Table.2 Corrosion parameters obtained from weight loss data for carbon steel in 1N HCl (25°C) containing different concentrations of 4 ABHMPT

Concentration ($mg.L^{-1}$)	Corrosion rate ($mg.cm^{-2}.h^{-1}$)	Inhibition efficiency *IE(%)*
Blank	914	--
50	230	74.83
100	82	91.02
200	28	96.93
300	10	98.90

It can be observed that inhibition efficiency increased with increases in concentration for both the inhibitors. Inhibition efficiency of 4-ABHMPT was estimated to be better than 74.83 per cent in 1N HCl even at very low concentration (50 $mg.l^{-1}$), and the optimum concentration for maximum efficiency was found to be 300 $mg.l^{-1}$.

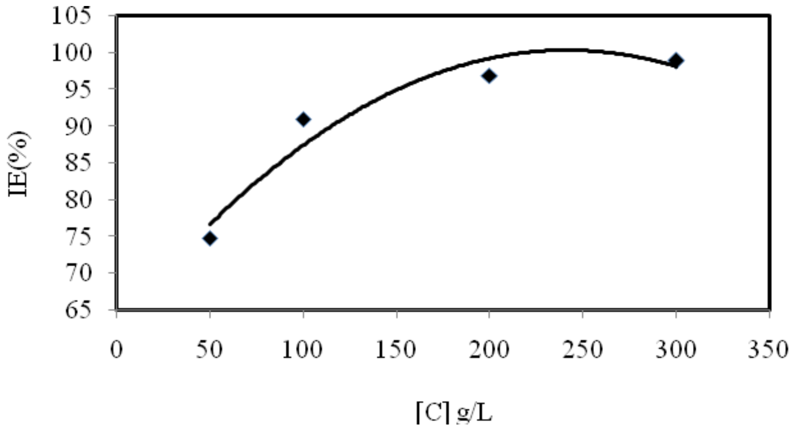

Figure.2: *Inhibition efficiency of 4-ABHMPT on mild steel in N HCl as a function of concentration*

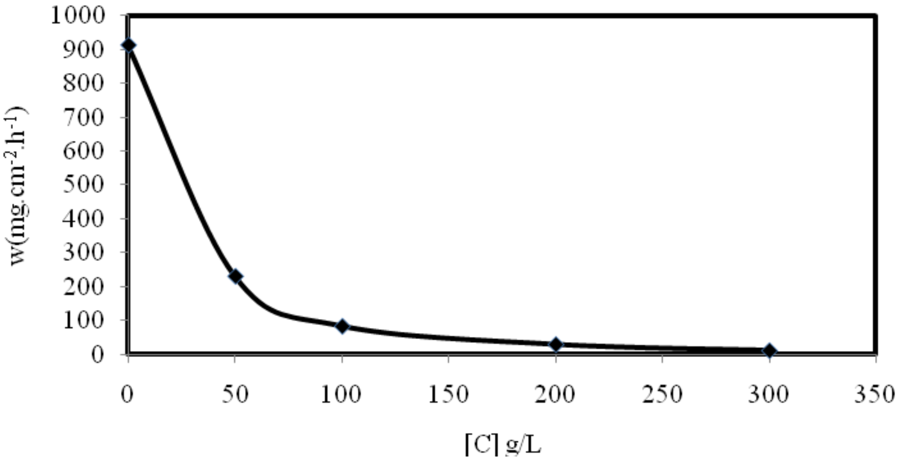

Figure.3: *Corrosion rate of mild steel in 1N HCl as a function of inhibitor concentration*

Temperature can influence the interaction between the carbon steel and acidic media without and with the inhibitor. Table.3 presents the corrosion rate and the inhibition efficiency for carbon steel in 1N HCl in the absence and presence of 300 mgl^{-1} of the inhibitor in the temperature range 25–55°C. The values of inhibition efficiency of the inhibitor were very similar over the temperature range studied. The corrosion rate for carbon steel increased rapidly with temperature in the absence of the inhibitor. The result confirmed that this Triazole compound can act a corrosion inhibitor for carbon steel in the range of temperature studied.

Table.3 The influence of temperature on the corrosion parameters for mild steel in the absence and presence of 300 mg.l-1 4-ABHMPT from weight-loss measurements

Temperature (K)	Concentration of 4-ABHMPT ($mg.L^{-1}$)	Corrosion rate ($mg.cm^{-2}.h^{-1}$)	Inhibition efficiency *IE%*
298	0.0	914	-
	300	10	98.90
308	0.0	1812	-
	300	270	85.09
318	0.0	2275	-
	300	532	76.61
328	0.0	2985	-
	300	808	72.93

The corrosion can be regarded as an Arrhenius-type process. The values of activation energy *Ea* were calculated using the Arrhenius equation:

$$Ln(w) = A - \frac{Ea}{RT} \qquad (3)$$

Where *Ea* is the apparent activation energy for the corrosion process, A is the Arrhenius pre-exponential constant.

When the corrosion rate data obtained from the weight-loss measurements in Table 4 is used and its Ln(*w*) is plotted vs 1/T, straight lines are obtained and values of *Ea* are given as the slopes of the lines. The values of Ea for mild steel in 1N HCl, in the absence and presence of 300 mg 4-ABHMPT, are then obtained.

***Table.4** variation of the Ln(w) in the presence and absence of the inhibitor*

T(K)	1000 /T	Ln (w_0)	Ln (w)
298	3,35	6,82	2,3
308	3,25	7,5	5,6
318	3,14	7,73	6,28
328	3,05	8	6,69

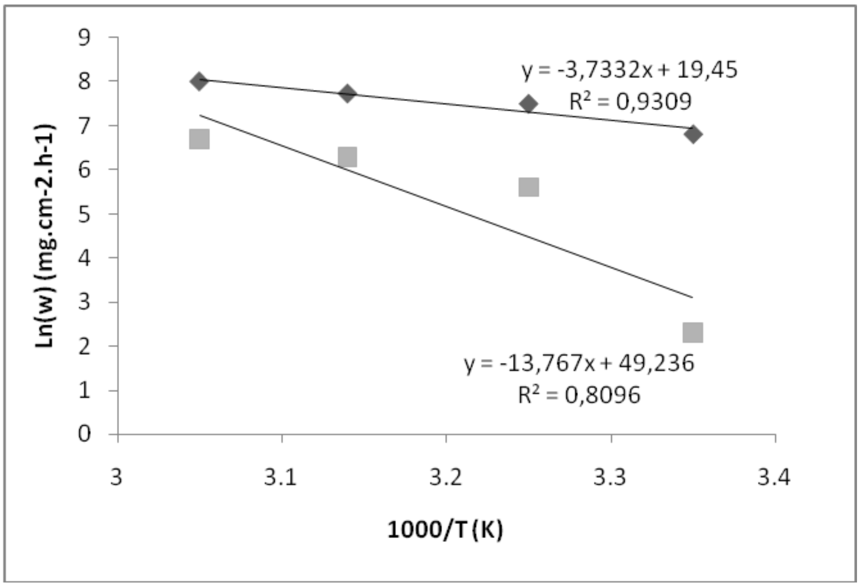

***Figure.4:** Ln(w) vs 1/T for mild steel in 1N HCl in the absence (bleu) and in the presence (rouge) of 300 mg of 4-ABHMPT*

Values of the *Ea* in presence and absence of the inhibitor are 31 and 114 kJ.mol^{-1}, respectively. The decrease in apparent free energy of activation in the presence of the triazole compound may be attributed to the chemisorptions of the inhibitor on mild steel surface, and the corrosion process corresponds to a different mechanism of steel dissolution in the presence of the inhibitor **[28]**.

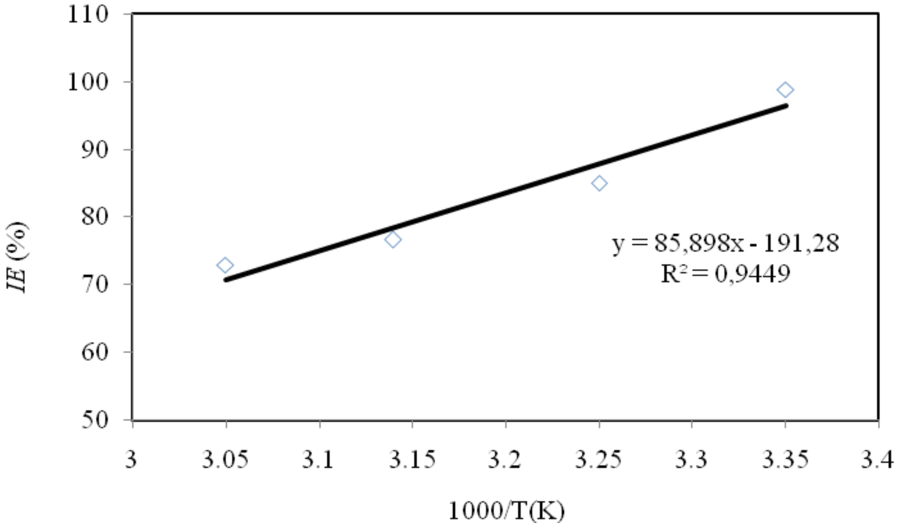

Figure.5: *Inhibition efficiency of 300 mg.L^{-1} of 4-ABHMPT on mild steel in 1N HCl as a function of temperature.*

IV. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Impedance diagrams obtained for frequencies ranging from 10kHz to 20 mHz at open circuit potential for carbon steel in 1N HCl in the absence and in the presence of various concentrations of 4-ABHMPT are shown in Figure 2. The diagrams are not perfect semicircles. The distortion has been attributed to frequency dispersion **[29]**.The fact that impedance diagrams have an approximately semicircular appearance shows that the corrosion of steel is controlled by a charge transfer process. Table.5 gives the

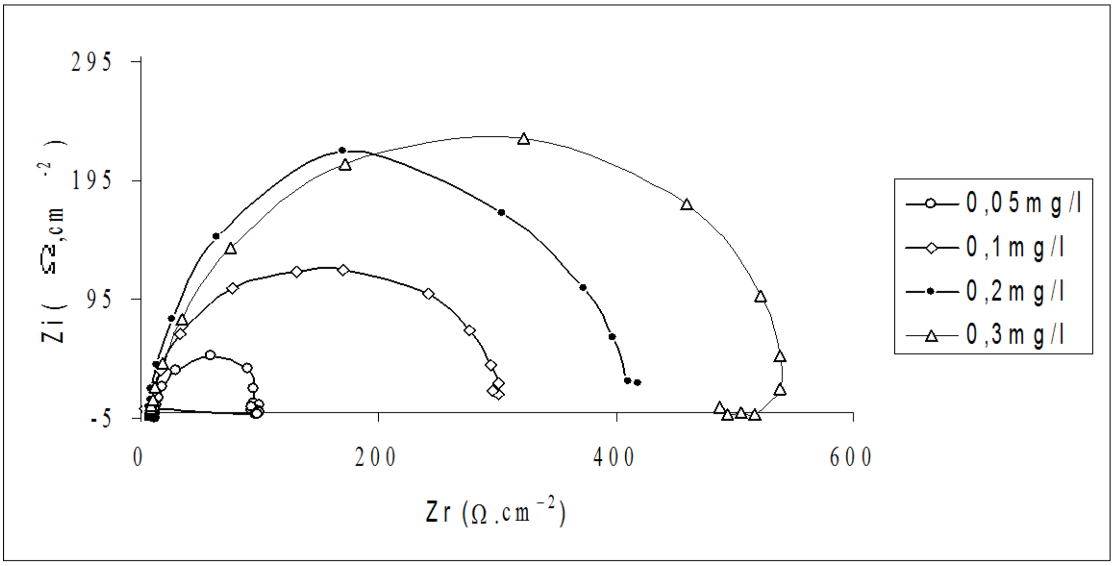

Figure.6: Nyquist diagrams of mild steel in 1M HCl without and with different concentrations of 4-ABHMPT

Values of the charge transfer resistance R_t, double layer capacitance C_{dl}, and inhibition efficiency obtained from the above plots. It could be seen from Table V that the charge-transfer resistances, R_t,, increase with increasing concentration of 4-ABHMPT and the inhibiting power is higher. A large charge-transfer resistance is associated with a slower corroding system **[30]** Furthermore, a better protection provided by an inhibitor is associated with a decrease in capacitance of the metal **[31]**. The decrease in Cdl, which results from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the triazole act by adsorption on the metal/solution interface [32]. As could be seen from Table V Cdl is decreased with increasing triazole concentration. The greatest inhibition was observed at concentration of 300 mg.l^{-1}. The impedance study also confirmed the inhibiting character of 4-ABHMPT obtained with weight loss measurements.

Adsorption isotherms

The results obtained with different concentrations are summarized in table 5.

Table.5 *Impedance parameters for corrosion of mild steel in 1 N HCl with different concentrations of 4-ABHMPT.*

4-ABHMPT(mg/l)	R_t (Ωcm^{-2})	C_{dl}(μFcm^{-2})	*IE*(%)	θ
Blank	16.31	517.14	--	--
50	100.86	49.71	83.83	0.90
100	302.29	44.47	94.61	0.91
200	410.16	40.26	96.04	0.92
300	550.00	22.40	97.06	0.96

Plots of R_t and C_{dl} against the concentration of 4-ABHMPT are shown in Figure.6. The figures.6 indicating that higher the concentration of inhibitor, the higher the charge transfer resistance and more the double layer capacitance decreases, up to a concentration of 300 mg. l^{-1}, where it is equal to 550 R_t (Ωcm^{-2}) and C_{dl} is equal to 22.40 (μFcm^{-2}) .

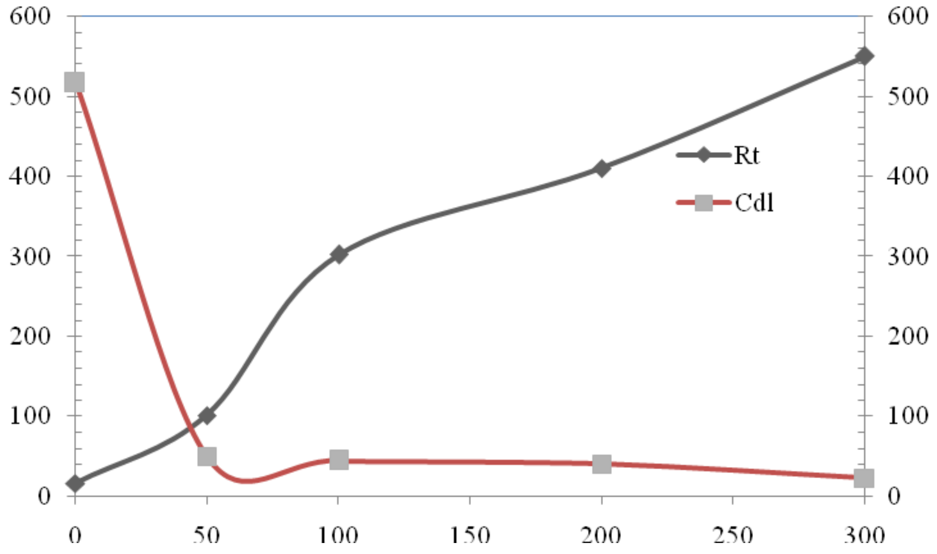

Figure.7: The double layer capacitance and the charge transfer resistance for mild steel in 1N HCl containing different concentrations of 4-ABHMPT

The adsorption isotherm : Surface coverage (θ) values have been obtained from the values of inhibition efficiency for different concentrations of 4-ABHMPT. It can be seen from Figure 8 that a plot of log C vs θ of the compound gives a straight line for both the acids. This observation clearly brings out the fact that the adsorption of 4-ABHMPT on the metal surface from both the acids obeys Lagmuir's adsorption.
In order to obtain the adsorption isotherm, the degree of surface coverage (θ) for the various concentrations of the inhibitor has been calculated using the following equation:

$$\theta = \frac{C_{dl^\circ} - C_{dl_{inh}}}{C_{dl^\circ}} \qquad (4)$$

where C_{dl° and $C_{dl(inh)}$ are the double layer capacitance in absence and presence of the inhibior, respectively.

The values of θ were tested graphically for fitting a suitable adsorption isotherm. The plot of Cinh/θ versus yields a straight line with slope equal the unity as shown in Fig. VII. The experimental results are in good agreement with the Langmuir adsorption isotherm, which is represented by the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (5)$$

The mechanism of the inhibition of corrosion of carbon steel in 1N HCl may be explained on the basis of adsorption. In aqueous acidic solutions, the investigated triazole can exist as cationic species. These cations can adsorb on the cathodic sites of the carbon steel surface and cause a decrease in the rate of evolution of hydrogen. The results of the present work indicate that triazole compounds adsorb on the metal surface through a process of chemisorption. The inhibitor film could prevent the attack of Cl^- ions, thereby retaining the M-O-M and M-O-H…O-M bonds.The adsorption of the protonated form of the triazole onto the iron surface occurs by establishing “donor/acceptor” interactions between the π electrons of the heterocyclic compound and the vacant “d “orbitals of iron surface atoms, which involves displacement of water molecules from the metal surface and the sharing of electrons between the nitrogen atoms and the metal surface.

The adsorption of organic substance (triazole in this case) at the metal/solution interface may be written according to the following displacement reaction [33]:

$$\textit{Surfactant (soluble)} + nH_2O \rightarrow \textit{surfactant} + nH_2O \qquad (6)$$

Where *n* is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed.

Clearly, the value of *n* depends on the cross-section area of the triazole molecule. Adsorption of the triazole molecule occurs because the interaction energy between the inhibitor and the metal surface is higher than the interaction energy between water molecules and the metal surface **[23]**.

The compound 4-ABHMPT has an additional electron releasing group ($-OCH_3$), which probably may also be attached there by accounting for the observed high *IE*.

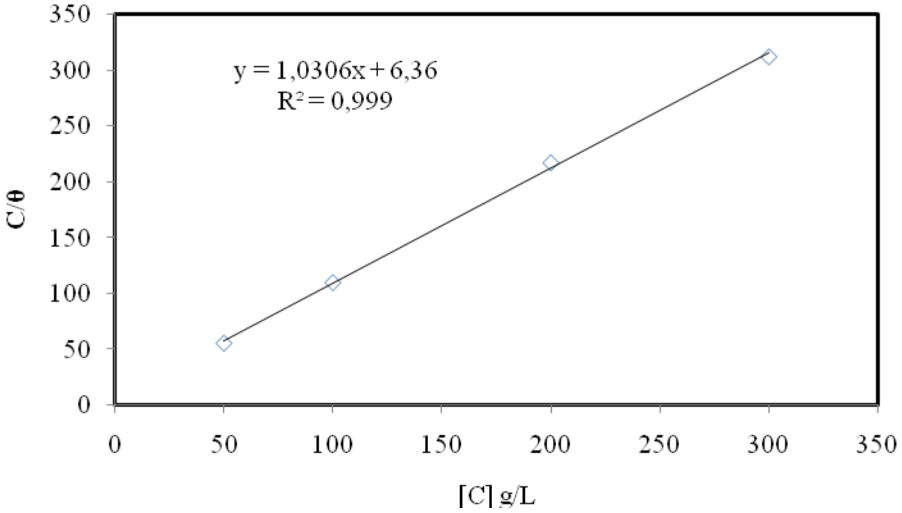

Figure.8: *Langmuir adsorption plots for mild steel in 1N HCl containing different concentrations of 4-ABHMPT: (a) the charge transfer resistance, (b) the double layer capacitance.*

V. CONCLUSION

4-ABHMPT behaves as an effective inhibitor for carbon steel corrosion in hydrochloric acid media. The inhibition efficiency of the inhibitor increases with the inhibitor concentration, but is temperature-independent. The adsorption of the inhibitor compound on carbon steel surface obeys Langmuir isotherm.

The results of (EIS) measurements indicated that, as the concentration of the inhibitor increases, the charge transfer resistance (*R*t) is increased, while the double layed capacitance is decreased. The inhibition is due o the adsorption of the inhibitor molecules on mild steel surface and blocking is active sites.

The results obtained from different experimental studies are in good agreement.

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