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3,5-bis(*n*-Hydroxyphenyl)-4-amino-1,2,4-triazoles and 3,5-bis(*n*-aminophenyl)-4-amino-1,2,4-triazoles: a new class of corrosion inhibitors for mild steel in 1 M HCl medium

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Abstract

A new class of corrosion inhibitors, namely, 3,5-bis(*n*-hydroxyphenyl)-4-amino-1,2,4-triazoles and 3,5-bis(*n*-aminophenyl)-4-amino-1,2,4-triazoles which have been labelled *n*-HPAT and *n*-APAT has been synthesized. The influence of aminotriazoles on the corrosion of mild steel in 1 M HCl has been studied using weight loss and electrochemical impedance spectroscopy. Results obtained show that these compounds are very good anodic inhibitors. The adsorption of these aminotriazoles is found to obey Langmuir adsorption isotherm.

1. Introduction

The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [1]. Acid solutions are generally used for the removal of rust and scale in several industrial processes. Inhibitors are generally used in these processes to control the metal dissolution. HCl was widely used in the pickling of steel and ferrous alloys. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. The influence of organic compounds containing nitrogen, such as amines, oxygen, such as phenols, on the corrosion of steel, in acidic solutions, has been investigated by several workers [2, 3]. The existing data show that most organic inhibitors act by adsorption on the metal surface. This phenomenon is influenced by the nature and surface charge of metal, by the type of aggressive electrolyte and by the chemical structure of inhibitors [4]. The most important prerequisites for compounds to be efficient inhibitors are that substances should chemisorb on the metal surface, have a high adsorption energy on the metal surface, and the barrier layer thus formed should increase the inner layer thickness.

Aminotriazoles have special affinity toward metal surfaces, displacing water molecules on the surface. In addition, the aminotriazoles possesses an abundance of π-electrons and unshaped electron pairs on the nitrogen and oxygen atoms which can interact with d-orbitals of iron to provide a protective film. The aim of this paper is to study the inhibiting action of a new class of organic compounds containing a triazole heterocycle and aromatic rings. The electrochemical behaviour of mild steel in HCl media in the absence and presence of inhibitor have been studied by electrochemical impedance spectroscopy and gravimetric methods.

2. Experimental details

2.1. *Inhibitor*

Figure 1 shows the molecular structure of the investigated compounds which have been labelled *n*-HPAT and *n*-APAT where $n = 2$, 3 and 4.

The aminotriazoles derivatives *n*-HPAT and *n*-APAT were synthesized according to a slightly modified experimental procedure [5]. A mixture of *n*-hydroxy or *n*-aminobenzonitrile (10^{-2} mol), hydrazine hydrate (2×10^{-2} mol) and hydrazinium sulfate (2×10^{-2} mol) was warmed on a water bath for 3 h. Aqueous hydrochloric acid (110 ml, 2 M) was slowly added to the reaction mixture and was then boiled for 15 min. The solution was cooled to 0 °C and made alkaline with ammonia solution ($d = 0.88$). The white precipitate was collected and crystallized from ethanol in

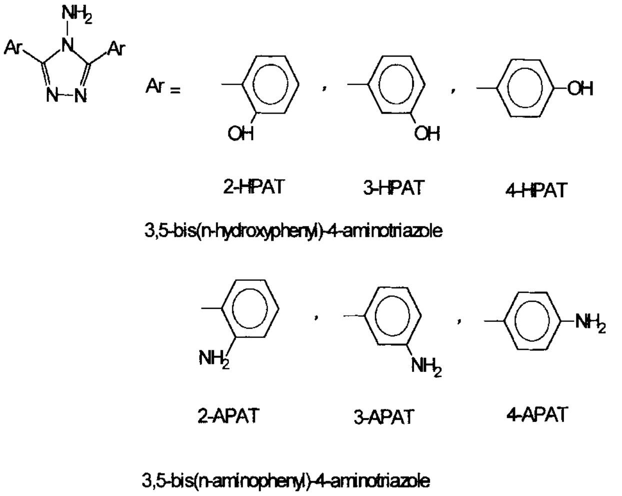

Fig. 1. Chemical formulae of the investigated HPAT and APAT derivatives.

colourless needles. The compounds structures were confirmed by ^1H nuclear magnetic resonance spectroscopy (NMR).

(i) *2-HPAT.* Yield 70%; m.p. 252 °C.
^1H-NMR data (in DMSO): 6.2(s, NH_2, 2H); 7.0(m, 4H); 7.4(m, 2H); 8.1(m, 2H); 11.3 (s, 2OH, 2H).

(ii) *3-HPAT.* Yield 71%; m.p. 332 °C.
^1H-NMR data (in DMSO): 6.2(s, NH_2, 2H); 6.9(d, 2H); 7.3(t, 2H); 7.4 (s + d, 4H); 9.8(s, 2OH, 2H).

(iii) *4-HPAT.* Yield 74%; m.p. 282 °C.
^1H-NMR data (in DMSO): 6.1(s, NH_2, 2H); 6.9(d, 4H); 7.8(d, 4H); 10.0(s, 2OH, 2H).

(iv) *2-APAT.* Yield 73%; m.p. 250 °C.
^1H-NMR data (in DMSO): 6.1(s, $2NH_2$, 4H); 6.3(s, NH_2, 2H); 7.0(m, 4H); 7.4(m, 2H); 8.0(m, 2H).

(v) *3-APAT.* Yield 76%; m.p. 232 °C.
^1H-NMR data (in DMSO): 5.2(s, $2NH_2$, 4H); 6.1(s, NH_2, 2H); 6.5(m, 2H); 6.7(m, 2H); 7.2(m, 4H).

(vi) *4-APAT.* Yield 78%; m.p. 282 °C.
^1H-NMR data (in DMSO): 5.5(s, $2NH_2$, 4H); 6.0(s, NH_2, 2H); 6.6(d, 4H); 7.7(d, 4H).

2.2. *Specimens*

Mild steel strips containing 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S and the remainder iron were used for the gravimetric and electrochemical measurements. The specimens were mechanically polished using different grades of emery paper (120–600–1200). They were subsequently washed with bidistilled water, washed in an ultrasonic bath with ethanol and then dried at room temperature. The aggressive solutions used were made of AR grade HCl. Appropriate concentrations of acid were prepared using bidistilled water.

2.3. *Corrosion weight loss tests*

For weight loss measurements, rectangular steel specimens of size 5 cm × 2 cm × 0.025 cm were immersed in 200 ml of inhibited and uninhibited solutions and allowed to stand for 24 h at 30 °C in air without bubbling.

2.4. *Electrochemical impedance spectroscopy (EIS)*

EIS measurements were carried out at E_{corr} after immersion on standing in air atmosphere without bubbling with the electrochemical system (Tacussel) which included a digital potentiostat model Z computer. Square sheets of mild steel of size 5 cm × 5 cm × 0.025 cm exposing a circular surface of 7.55 cm^2 to the solution were used as the working electrode. After the determination of steady-state current at a given potential, sine wave voltages (10 mV) peak to peak, at frequencies between 100 kHz and 10^{-2} Hz, were superimposed on the potential. The measurements performed at rest potentials after 20 h of immersion were automatically controlled with the aid of computer programs.

3. Results and discussion

3.1. *Corrosion weight loss measurements*

The percentage inhibition efficiency of the triazoles for the corrosion of mild steel was calculated as follows:

$$\eta = \left[\frac{W_0 - W}{W_0}\right] \times 100 \tag{1}$$

where w_0 and w are the values of the weight loss of steel after immersion in solutions without and with inhibitor, respectively.

Table 1 gives values of inhibition efficiencies obtained from the weight loss for 300 mg dm^{-3} for various isomers of 4-HPAT and 4-APAT in 1 M HCl. The efficiency is superior at 97% in 1 M HCl.

3.2. *Electrochemical impedance spectroscopy (EIS)*

The corrosion behaviour of mild steel in acidic solution in the presence of aminotriazoles was investigated by EIS

Table 1. Inhibition efficiencies of mild steel for 300 mg dm^{-3} of various isomers of 4-HPAT and 4-APAT in 1 M HCl from weight loss measurements

Inhibitor	Inhibition efficiency, η /%
2-HPAT	97.70
3-HPAT	97.70
4-HPAT	99.90
2-APAT	98.50
3-APAT	99.00
4-APAT	99.00

at 30 °C after 20 h immersion. The locus of the Nyquist plots was regarded as one part of a semicircle. The equivalent circuit models employed for this system are as previously reported [6]. The impedance diagrams obtained are not perfect semicircles, and this difference has been attributed to frequency dispersion [7]. The charge transfer resistance, R_t values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Haruyama and Tsuru [8]. Percentage inhibition efficiencies obtained from electrochemical impedance measurements are calculated as follows:

$$\eta_{\mathrm{Rt}} = \left(\frac{R_{t_0}^{-1} - R_t^{-1}}{R_{t_0}^{-1}}\right) \times 100 \qquad (2a)$$

$$\eta_{\mathrm{cdl}} = \left[\frac{C_{\mathrm{dl}_0} - C_{\mathrm{dl}}}{C_{\mathrm{dl}_0}}\right] \times 100 \qquad (2b)$$

where R_{t_0} and R_t are the values of charge transfer resistance and C_{dl_0} and C_{dl} are the double layer capacitance for mild steel in 1 M HCl, respectively, without and with inhibitor.

Electrochemical parameters established with the Nyquist diagram, obtained with and without addition of 300 mg dm^{-3} for various isomers of HPAT and APAT in 1 M HCl, are listed in the Table 2. The inhibition efficiencies obtained from weight loss and electrochemical impedance spectroscopy measurements are in good agreement (Tables 1 and 2).

Tables 3 and 4 give values of electrochemical parameters for mild steel in 1 M HCl in the presence of different concentration of 4-HPAT and 4-APAT.

Table 3 shows that the inhibition efficiency increases with increasing concentration of 4-HPAT and reaches a level of 98.97% for an inhibitor concentration of 300 mg dm^{-3}. The values of corrosion potential shift in the positive direction as the inhibitor concentration increases. This indicates the presence of an anodic inhibitor.

Table 2. Impedance parameters for the corrosion of mild steel for 300 mg dm^{-3} of various isomers of HPAT and APAT in 1 M HCl

Inhibitor	R_t /Ω cm^2	C_{dl} /μF cm^{-2}	E vs SCE /mV	η_{R_t} /%	$\eta_{C_{\mathrm{dl}}}$ /%
2-HPAT	715.50	78.90	–459	97.70	84.74
3-HPAT	715.90	26.95	–459	97.72	94.79
4-HPAT	1583.33	35.75	–471	98.97	93.10
2-APAT	715.50	78.90	–443	97.72	84.74
3-APAT	967.14	51.80	–438	98.31	89.98
4-APAT	1007.9	34.80	–450	98.38	93.27

Table 3. Impedance parameters for the corrosion of mild steel in 1 M HCl containing different concentrations of 4-HPAT

Inhibitor /mg dm^{-3}	R_t /Ω cm^2	C_{dl} /μF cm^{-2}	E vs SCE /mV	η_{R_t} /%	$\eta_{C_{\mathrm{dl}}}$ /%
Blank	16.30	517.14	–496		
50	164.16	97.19	–478	90.16	81.20
100	450	53.50	–476	96.37	86.65
200	660	46.77	–476	97.53	90.94
300	1583.33	35.75	–471	98.97	93.10

Table 4. Impedance parameters for the corrosion of mild steel in 1 M HCl containing different concentrations of 4-APAT

Inhibitor /mg dm^{-3}	R_t /Ω cm^2	C_{dl} /μF cm^{-2}	E vs SCE /mV	η_{R_t} /%	$\eta_{C_{\mathrm{dl}}}$ /%
Blank	16.30	517.14	–493		
50	389.19	43.60	–478	95.80	91.60
100	546.99	41.50	–474	97.02	91.97
200	967.14	35.46	–469	98.31	93.14
300	1007.90	34.80	–452	98.50	93.27
500	1741.9	29.40	–450	99.06	94.31

Plots of R_t^{-1} and C_{dl} against the concentration of 4-APAT are shown in Figs 2 and 3. Figures 2 and 3 are similar, 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 dm^{-3}, where it remains almost constant.

From Fig. 4 it can be seen that inhibition efficiencies obtained from C_{dl} and R_t are in good agreement. Similar behaviour is observed in 4-APAT (Figs 5, 6 and 7).

The adsorption of HPAT and APAT on the metal surface occurs either directly, on the basis of donor–acceptor interactions between the π-electrons of the heterocycle compound and the vacant d-orbitals of iron surface atoms, or interaction of HPAT or APAT with already adsorbed chloride ions [9]. The performance of aminotriazoles in 1 M HCl can be explained as follows. In aqueous acidic solutions, the aminotriazole exists either as neutral molecules or in the form of cations. In the form of neutral molecule, the aminotriazole, sharing of electrons between the nitrogen atoms and the metal surface, could be adsorbed on the surface, and leads to the displacement of water [10]. The aminotriazole can

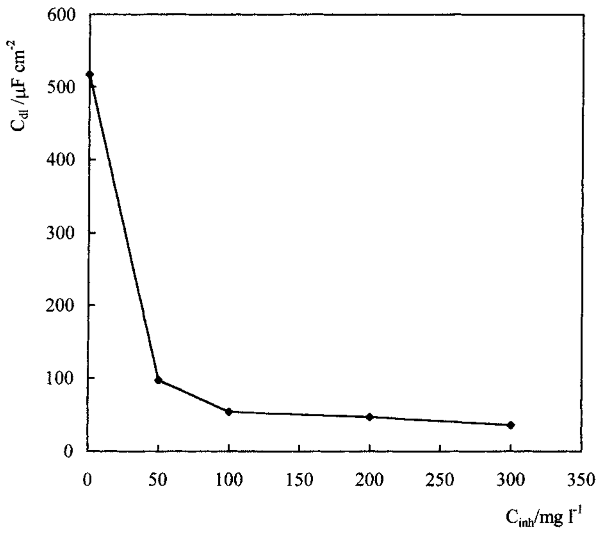

Fig. 2. The double layer capacitance for mild steel in 1 M HCl containing different concentrations of 4-HPAT.

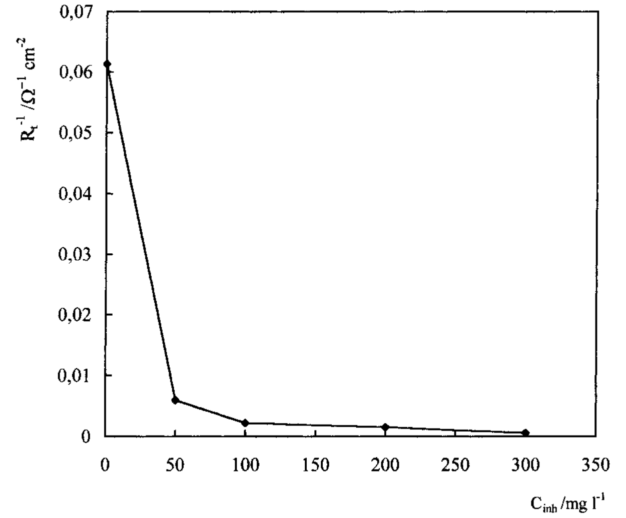

Fig. 3. The inverse charge transfer resistance for mild steel in 1 M HCl containing different concentrations of 4-HPAT.

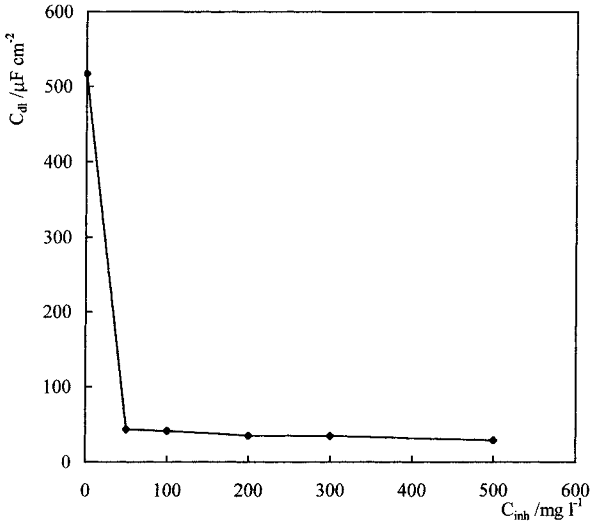

Fig. 5. The double layer capacitance for mild steel in 1 M HCl containing different concentrations of 4-APAT.

also adsorb through electrostatic interactions between the positively charged nitrogen atom and the negatively charged metal surface [11]. In addition, these molecules possess an abundance of π-electrons and unshared electron pairs which interact with the d-orbitals of iron to provide a protective film. The ability of the molecule to chemisorb on the iron surface is dependent on the position of the amino or hydroxy group on the aromatic substituent (Tables 1 and 2). The highest percentage inhibition efficiency values are calculated for 4-HPAT and 4-APAT both from weight loss and charge transfer resistance data. The strong electron donor character of the substituent enhances the electronic density near the aminotriazole. It is noticeable that the use of potentially chelating agent such as 2-HPAT and 2-APAT does not produce a notable improvement compared to the isomer nonchelating molecules (3 and 4-HPAT, 3 and 4-APAT), which suggests that, in the present case, the ability to form coordination complexes does not occur.

3.3. *Study of the adsorption phenomenon*

The adsorption of the organic compounds can be described by two main types of interaction: physical adsorption and chemisorption. These are influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte.

If it is supposed that the adsorption of this inhibitor follows the Langmuir adsorption isotherm, the degree of surface coverage (θ) is given by

$$\theta = \frac{b\,C_{\mathrm{inh}}}{1 + b\,C_{\mathrm{inh}}} \tag{3}$$

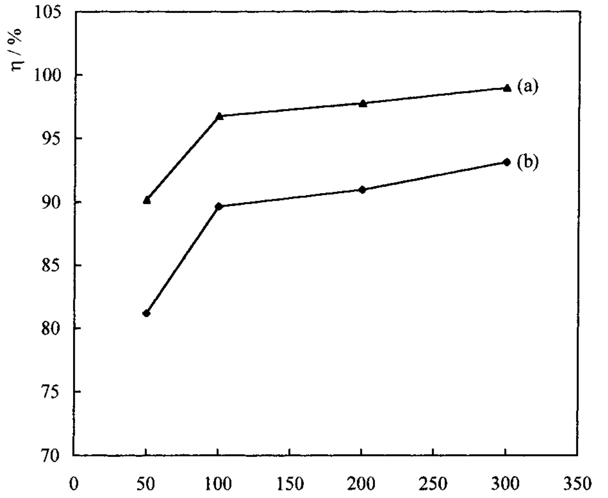

Fig. 4. Inhibition efficiency (η) for mild steel in 1 M HCl containing 4-HPAT: (a) the charge transfer resistance, (b) the double layer capacitance.

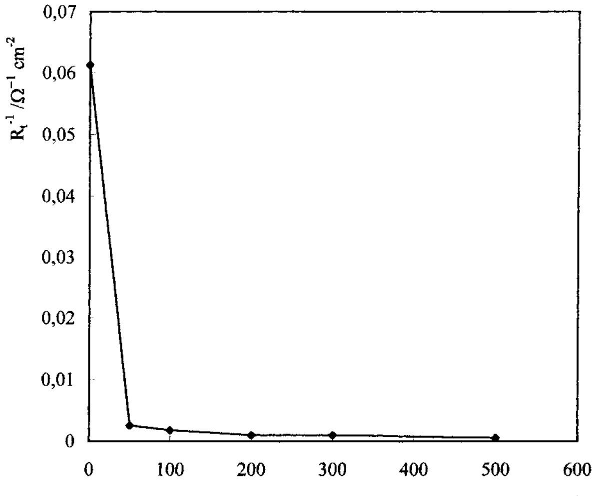

Fig. 6. The inverse charge transfer resistance for mild steel in 1 M HCl containing different concentrations of 4-APAT.

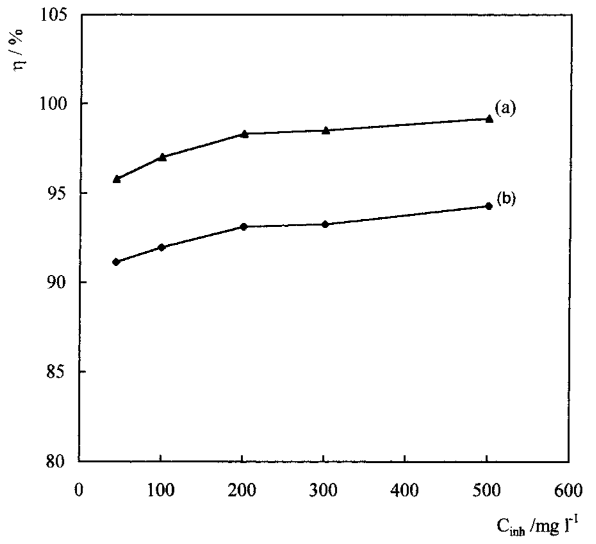

Fig. 7. Inhibition efficiency (η) for mild steel in 1 M HCl containing 4-APAT: (a) the charge transfer resistance, (b) the double layer capacitance.

where *b* designates the adsorption coefficient. The degree of surface coverage for different concentrations of 4-HPAT and 4-APAT in 1 M HCl may be evaluated from impedance measurements using the following equations:

$$\theta = \frac{C_{\mathrm{dl}_0} - C_{\mathrm{dl}}}{C_{\mathrm{dl}_0} - C_{\mathrm{dl}_{\mathrm{sat}}}}$$
$$\theta = \frac{R_{\mathrm{t}_0}^{-1} - R_{\mathrm{t}}^{-1}}{R_{\mathrm{t}_0}^{-1} - R_{\mathrm{t}_{\mathrm{sat}}}^{-1}} \qquad (4)$$

The surface coverages (θ) were tested graphically to fit a suitable adsorption isotherm. The plot of $C_{\mathrm{inh}}\ \theta^{-1}$ against the concentration of 4-HPAT and 4-APAT yields straight lines showing that the adsorption of 4-HPAT and 4-APAT from 1 M HCl on the mild steel surface obeys a Langmuir adsorption isotherm (Figs 8 and 9).

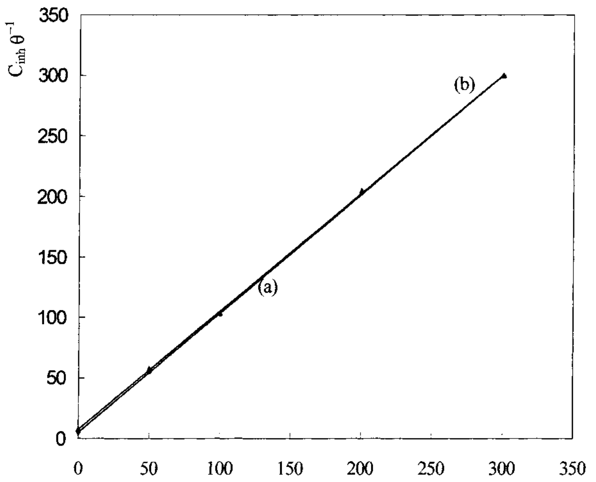

Fig. 8. Langmuir adsorption plots for mild steel in 1 M HCl containing different concentrations of 4-HPAT: (a) the charge transfer resistance, (b) the double layer capacitance.

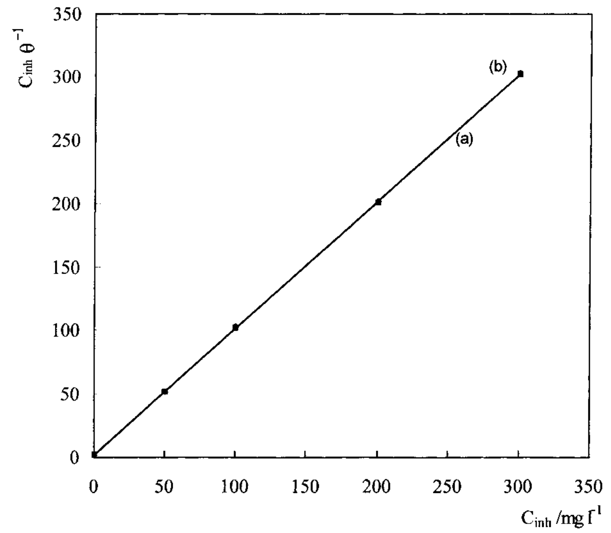

Fig. 9. Langmuir adsorption plots for mild steel in 1 M HCl containing different concentrations of 4-APAT: (a) the charge transfer resistance, (b) the double layer capacitance.

The value of adsorption coefficient (*b*) for mild steel in 1 M HCl in the presence of 4-HPAT is about 3.9×10^{-2} dm^{3} mol^{-1} and 0.15 dm^{3} mol^{-1} for 4-APAT, which is in good agreement with the values of inhibition efficiency obtained from the weight loss and impedance spectroscopy measurements. Thus, the inhibition efficiency increases with increasing adsorption coefficient.

4. Conclusion

It can be concluded that:

(i) *n*-HPAT and *n*-APAT inhibit the corrosion of mild steel in 1 M HCl medium.
(ii) *n*-HPAT and 4-APAT behave as anodic inhibitors in HCl.
(iii) Strong adsorption of *n*-HPAT and *n*-APAT molecules on the active sites of a metal surface suppress the dissolution reaction and adsorption leads to the formation of a protective film which grows with increasing exposure time.
(iv) The adsorption of *n*-HPAT and *n*-APAT on the mild steel surface from 1 M HCl obeys a Langmuir adsorption isotherm.
(v) The inhibition efficiency increases with increasing value of the adsorption coefficient.

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