

Full Paper

Investigation of Inhibition Effect of 1-(aminoN-phenyl methanethio) thiosemicarbazide on Carbon Steel Corrosion in Acidic Solution: Adsorption Behavior Study using Fast Fourier Transform Continuous Cyclic Voltammetry

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Received: 29 December 2014 / Received in Revised form: 28 April 2014 /

Accepted: 1 May 2014 / Published online: 30 June 2014

Abstract- Corrosion inhibition of carbon steel in 1.0 M HCl solution by 1-(aminoN-phenylmethanethio)thiosemicarbazide (APTSC) was investigated by potentiodynamic polarization, Electrochemical Impedance Spectroscopy (EIS) and Fast Fourier Transform Continuous Cyclic Voltammetry (FFTCCV). Polarization studies revealed that APTSC is a mixed-type corrosion inhibitor. The results showed that the inhibition efficiency increased with increasing the inhibitor concentration and maximum inhibition was obtained 92% at 1.0×10^{-3} M of APTSC. EIS results confirmed that the inhibitor is adsorbed on the carbon steel surface, leading to increase the polarization resistance (R_p) and decrease the double layer capacitance. FFTCCV confirmed that the addition of inhibitor into the HCl solution decreased the rate of carbon steel corrosion. Also, it was found that after about 3400 s, the inhibitor reaches to its maximum surface coverage.

Keywords- Carbon steel, Corrosion inhibitor, Adsorption, FFTCCV

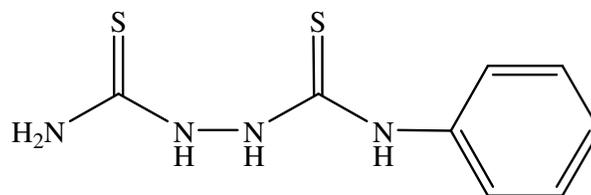
1. INTRODUCTION

Carbon steel is the primary metal used for structural applications because it has good strength, formability, abundance, and low cost [1]. Despite its relatively limited corrosion resistance, very large amounts of carbon steels are used in marine applications, nuclear and fossil fuel power plants, transportation, chemical processing, mining, and metal- processing equipment. All of these areas present unique corrosion problems, and subsequently, corrosion protection needs often an essential account when carbon or alloy steel is selected for a given structural application. It is well known that corrosion of steel surfaces can be controlled by the addition of chemical compounds to the aggressive medium, which is called inhibition and the compounds added are recognized as corrosion inhibitors. Among protection methods, inhibitors find their major uses in acid pickling solutions, acidic service environments, steam systems and neutral and near neutral aqueous solutions [2,3]. Usually, organic substances having N, S, or O atoms with free electron pairs are used as corrosion inhibitors of metals in acidic media [4-8]. Nowadays, the development of low-cost and eco-friendly inhibitors for steel is a subject that takes increasing considerations [9-11]. The conventional methods frequently used for corrosion studies are weight loss measurements and electrochemical methods. Because of the electrochemical nature of corrosion phenomena, the electrochemical techniques are so profitable in this field of studies. Excellent information has been achieved with linear polarization studies, Tafel plots and electrochemical impedance spectroscopy (EIS). FFTCCV technique has been previously used to determine different compounds with low detection limits [12-17]. But, this report is the first use of this technique in corrosion studies. Applying high potential sweep rates resulting in a large number of cyclic voltammograms, real time analysis and integration of current at a specified potential and time window make it possible to study the adsorption behavior of inhibitor, continuously. The aim of this work is the investigation of inhibition effect of 1-(aminoN-phenylm ethanethio) thiosemicarbazide (APTSC) on carbon steel corrosion in 1.0 M HCl solution. The inhibition mechanism and evaluation of the inhibitor performance are studied by three electrochemical techniques, potentiodynamic polarization, EIS and Fast Fourier Transform Continuous Cyclic Voltammetry (FFTCCV).

2. EXPERIMENTAL SECTION

2.1. Synthesize of inhibitor

A mixture of phenylisothiocyanate (1.0×10^{-2} mol), thiosemicarbazide (1.0×10^{-2} mol) and a catalytic amount of acetic acid was mixed and refluxed in ethanol (70 mL) for 2 h to obtain compound B. Then the solvent was evaporated to 20 mL. After cooling to room temperature, the product crystals were obtained. The molecular structure of investigated inhibitor is shown in Fig. 1.



1-(amino-N-phenylmethanethio)thiosemicarbazide (APTSC)

Fig. 1. Molecular structure of investigated compound

2.2. Carbon steel samples and solutions

A carbon steel sample containing C 0.326%, Si 0.235%, Mn 0.742%, P 0.0159%, Cr 0.0733%, Ni 0.0149%, Al 0.022%, S 0.0171%, Cu 0.129%, V 0.0018% and the rest iron, was used to construct the working electrode. Before doing each measurement, the electrode surface was polished with different grades of emery papers (which ended with the 1200 grit), degreased in ultrasonic bath with ethanol and acetone and finally rinsed with distilled water. The aggressive solution of 1.0 M HCl was prepared by dilution of 36% HCl from Merck with distilled water. In order to solve the solubility problems, the inhibitor solutions were prepared in 1.0 M HCl containing 5% v/v DMSO. Obviously, this volume of DMSO was also added to the blank solution.

2.3. Polarization measurements

Polarization studies were performed using an AUTOLAB model PGSTAT30 and a three-electrode set-up containing a Pt counter electrode (CE), an Ag/AgCl reference electrode (RE) and a carbon steel working electrode (WE). The working electrode was constructed from a cylindrical carbon steel bar mounted in epoxy resin to give an exposed surface of 5 mm diameter. Prior to obtaining polarization curves, the fresh surface of WE was immersed in the test solution for 45 minutes to reach a steady state open circuit potential (E_{ocp}). After reaching the OCP, the potential was swept from a more positive potential than E_{ocp} to a more negative potential than E_{ocp} at a scan rate of 1 mV/S. The potentiodynamic polarization curves were recorded using a personal computer, which was connected to the electrochemical instrument. The polarization data was analyzed using GPES electrochemical software.

2.4. EIS measurements

The electrochemical impedance measurements were performed using the same instrument and cell set-up used for the polarization measurements. The EIS experiments were carried out at E_{ocp} by superimposing a sinusoidal potential of 5 mV amplitude at frequencies between 10^5 - 5×10^{-2} Hz. EIS data were analyzed with FRA software.

2.5. FFTCCV experiments

To perform FFTCCV experiments, a set-up containing a PC equipped with a data acquisition board (PCL-818HG, Advantech. Co.) and a custom-made potentiostat was used with a three-electrode configuration matching the one used for polarization and EIS experiments. At each FFTCCV run, cyclic voltammograms were obtained repeatedly by sweeping the potential between an initial and a final potential that includes corrosion potential (E_{corr}). Although in the most reported works the effect of inhibition were studied at low potential scan rates, due to the instrument limitations, the CV measurements were carried out at 1 V/s, which was the lowest possible scan rate that could be used to collect kinetic data.

3. RESULTS AND DISCUSSIONS

3.1. Potentiodynamic evaluation

The Tafel polarization curves for carbon steel in 1.0 M HCl solution without and with different concentration of APTSC are shown in Fig. 2. The curves show that both anodic and cathodic branches of the Tafel plots for APTSC containing solutions shift to lower values of current density. Observing such lower current densities could be related to hindrance the anodic dissolution of Fe and cathodic evolution of H_2 by organic molecules adsorbed on the electrode surface.

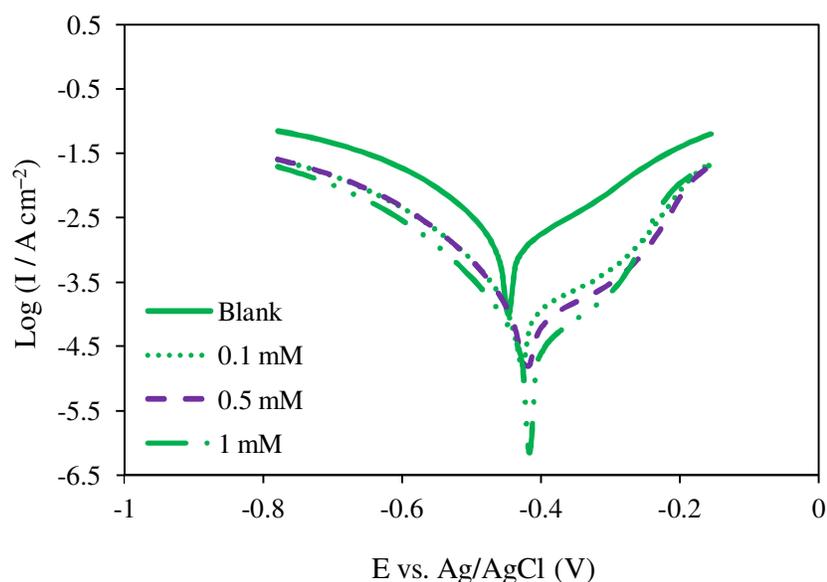


Fig. 2. Polarization curves of carbon steel electrode in 1.0 M HCl without and with different concentrations of APTSC

Table 1 illustrates the calculated electrochemical parameters of the corrosion process, namely potential of corrosion (E_{corr}), corrosion current density (I_{corr}) and the inhibition efficiencies (IE %) for the solution containing various concentrations of APTSC. The values of IE% were calculated according to the equation below:

$$\text{IE \%} = \frac{I_{\text{corr, uninhibit}} - I_{\text{corr, inhibit}}}{I_{\text{corr, uninhibit}}} \times 100 \quad (1)$$

where the $I_{\text{corr, uninhibit}}$ and $I_{\text{corr, inhibit}}$ are the corrosion current density in the absence and presence of the inhibitor, respectively. As shown in Fig. 2, the addition of APTSC causes the E_{corr} to displace toward more positive values of the potentials. In the literature, it was said that if the shift in E_{corr} resulting from addition of an inhibitor is more than 85 mV, the inhibitor could be anodic or cathodic type. But, if the displacement of E_{corr} is less than 85 mV, the added inhibitor could be mixed type [18-20]. Fig. 2 and Table 1 represent the maximum shift of the E_{corr} equals to 38 mV. Consequently, it can be concluded that APTSC is a mixed-type corrosion inhibitor.

Table 1. Polarization parameters for carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of APTSC

Inhibitor	C_{inh} (M)	$-E_{\text{corr}}$ (mV)	I_{corr} (μAcm^{-2})	$-b_c$ (mV dec^{-1})	b_a (mV dec^{-1})	IE (%)
Blank	–	455	461.30	137	111	-
APTSC	1.0×10^{-4}	422	74.81	146	131	83.8
	5.0×10^{-4}	428	59.57	142	135	87.1
	1.0×10^{-3}	417	39.35	133	145	91.5

3.2. EIS results

Fig. 3 demonstrates the Nyquist plots obtained for the carbon steel at the interface in 1.0 M HCl without and with different concentrations of APTSC. As shown in the figure, the Nyquist plots point only one capacitive loop, in which the diameter of the semicircle increases proportionally with the inhibitor concentration. Irregularities and heterogeneities of solid surfaces could cause frequency dispersion. So, the Nyquist plots of the carbon steel cannot accomplish a perfect semicircle. Also, these deviations could mostly be related to distribution of some physical processes and distribution of the reactivity [3,21]. Besides, the double layer on the interface of metal/solution cannot behave as a real capacitor.

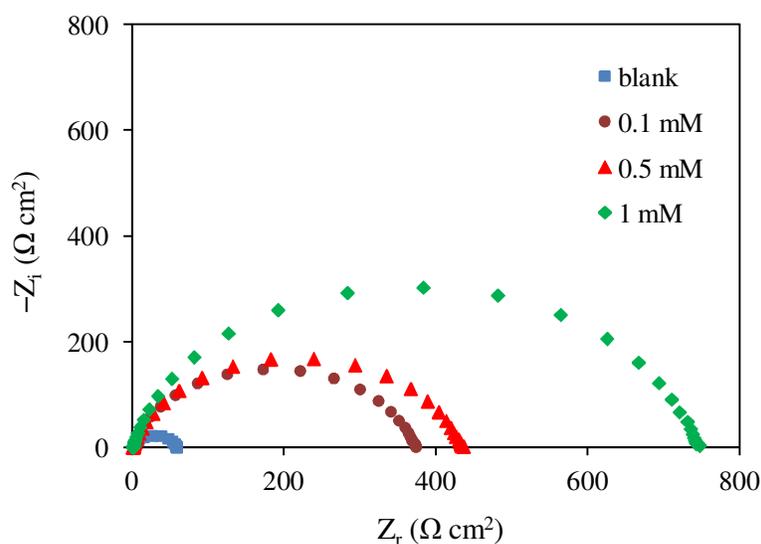


Fig. 3. Nyquist plots of carbon steel obtained in 1.0 M HCl in the absence and presence of various concentrations of APTSC

The equivalent circuit is shown in Fig. 4, in which the standard Randles circuit containing a solution resistance (R_s), a polarization resistance (R_p), and a constant phase element (CPE) is used to fit the experimental data. In corrosion systems, the use of CPE in replace of a double layer capacitance has been frequently reported [8,22-27]. The reason is to take account the inhomogeneities, frequency dispersion and distribution of some special characteristics of the system [28,29].

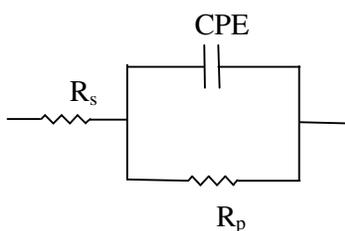


Fig. 4. Electrical equivalent circuit used for demonstrating carbon steel/solution interface.

The impedance function of a CPE takes the form [30]:

$$Z_{\text{CPE}} = Q^{-1}(j\omega)^{-n} \quad (2)$$

where Q is the magnitude of the CPE, n is the CPE exponent (phase shift), which could be used to explain the degree of surface inhomogeneity and non-ideality in capacitance behavior, j is the imaginary number and ω is the sine wave angular frequency ($\omega=2\pi f$, the frequency in Hz). The values of Q , n , R_s , R_p and $IE\%$ obtained using EIS method are listed in Table 2. In simple corrosion systems with one charge transfer control process, the polarization resistance, R_p , can be simply correlated with corrosion current density. The R_p values are used to calculate the $IE\%$ according to the equation below:

$$IE\% = \frac{R_{p,\text{inhibit}} - R_{p,\text{uninhibit}}}{R_{p,\text{inhibit}}} \times 100 \quad (3)$$

where $R_{p,\text{inhibit}}$ and $R_{p,\text{uninhibit}}$ are the polarization resistance of inhibited and uninhibited solutions, respectively. Table 2 shows that the values of R_p and therefore $IE\%$ enhance with an increase in APTSC concentration while Q value is generally decreased. It seems that declining of Q values is related to the replacement of adsorbed ions by the inhibitor molecules on the electrode surface. Also, the obtained data showed that with raising the concentration of the inhibitor, the value of R_p increases more significantly. These results confirm that APTSC molecules could lessen the corrosion rate of carbon steel in 1.0 M HCl via adsorption on the electrode surface, and produce a protective layer at the metal/solution interface. However, a comparison between the $IE\%$ values obtained by polarization method (Table 1) and EIS data (Table2) shows that the data obtained by two methods are in good agreement with each other.

Table 2. Electrochemical impedance parameters for carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of APTSC

Inhibitor	C_{inh} (M)	R_p ($\Omega \text{ cm}^2$)	n	CPE ($\mu\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	IE (%)
Blank	–	57.8	0.86	305.7	–
APTSC	1.0×10^{-4}	367.2	0.87	33.2	84.3
	5.0×10^{-4}	429.5	0.85	34.6	86.5
	1.0×10^{-3}	731.6	0.88	19.3	92.1

3.3. FFTCCV measurements

FFTCCV is used for studying continuously the adsorption of APTSC on the electrode surface. To calculate the response of the electrode, it is necessary to remove the background

CV from the CV of the sample. In fact, CV curves are recorded numerically by sampling current in equal time intervals. In the computer program, the value of current change over a potential range, E_1 and E_2 , was calculated by following equation [31-33]:

$$\Delta i(s,E)=i(s,E)-i(s_r,E) \quad (4)$$

where s is the sweep number, $i(s, E)$ represents the CV curve recorded during the s -th sweep and $i(s_r, E)$ is the reference CV curve.

Fig. 5a and b shows the typical differential CVs (all the cyclic voltammograms were subtracted from the reference CV) for the carbon steel electrode during 70 minutes immersion in 1.0 M HCl without (a) and with 5.0×10^{-4} M of APTSC. For each experiment, at first, the electrode was immersed for 70 minutes in the acidic solution. As expected, the net current change for the blank solution (up to 8.0 mA) is larger than the electrode in the inhibitor containing solution. The net corrosion currents change for the electrode in the solution containing APTSC is 3.8 mA. It means that the investigated thiosemicarbazide derivative reduce the corrosion current in real time. Overlay differential CVs in Fig. 5b show that at the start of the experiment, the slope of the maximum corrosion current change with time is relatively large and after 3400 s, it progressively becomes slighter until reaches to unchanging values. It could be correlated with the fact that the time needed for APTSC to reach its maximum surface coverage is around 3400 s.

As mentioned above, this method provides conditions for observing the corrosion inhibition process in time domain by following the amount of charge (ΔQ) that passes through the electrode during applying potential waveform. The following equation is theoretical approach for calculation of the charge under a cyclic voltammogram at the potential range E_1 to E_2 :

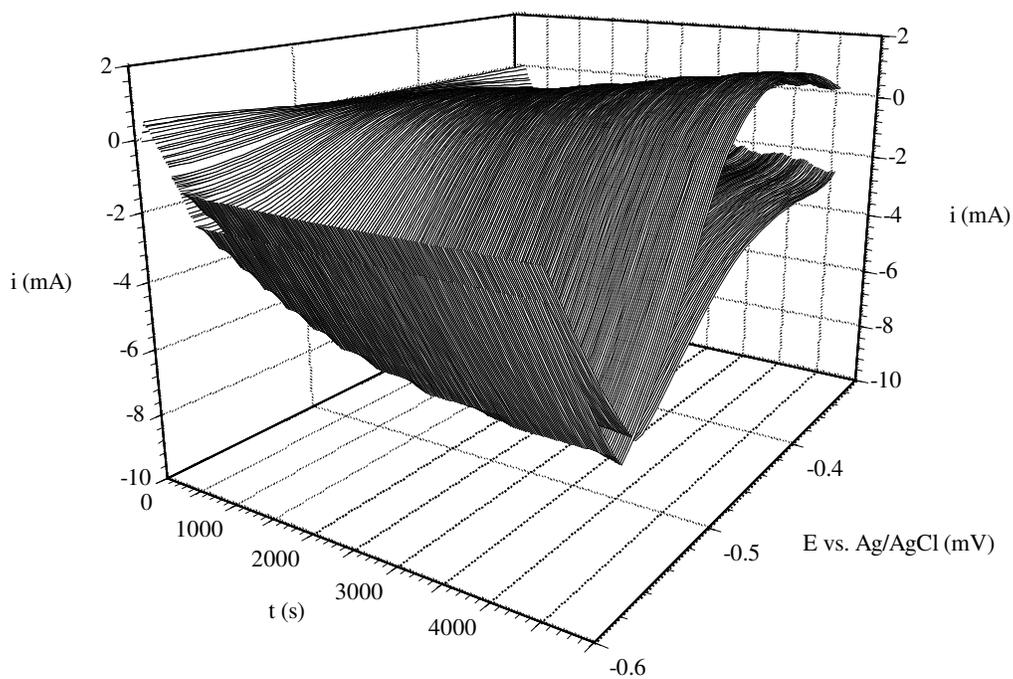
$$Q_t = \frac{1}{v} \int_{E_1}^{E_2} i(E) dE \quad (5)$$

where v is the scan rate.

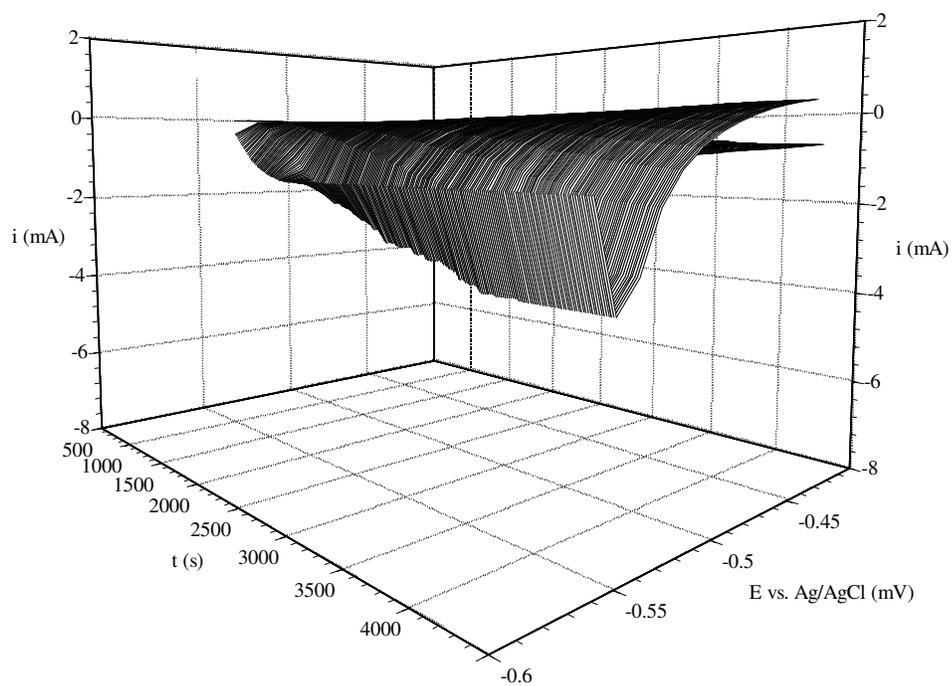
As previously mentioned, CV curves are recorded numerically by sampling current in equal time intervals. Therefore, we used the following equation to integrate the current over the potential range, E_1 to E_2 , and calculate ΔQ [34,35]:

$$\Delta Q(s,t) = \Delta t \left(\sum_{E=E_1}^{E=E_2} i(s,E) - \sum_{E=E_1}^{E=E_2} i(s_r,E) \right) \quad (6)$$

where s is the sweep number, t is the time period between subsequent sweeps, Δt is the time difference between two subsequent points on the CV curves, $i(s, E)$ represents the CV curve recorded during the s -th sweep and $i(s_r, E)$ is the reference CV curve. The reference CV curve was obtained by averaging three CVs recorded at the beginning of the experiment.



(a)



(b)

Fig. 5. Differential Continuous Cyclic Voltammogram of carbon steel electrode recorded during 70 minutes immersion in 1.0 M HCl without (a) and with 5.0×10^{-4} M of APTSC (b)

Fig. 6 represents the plot of ΔQ as a function of time for carbon steel electrode in 1.0 M HCl in the absence and presence of 5.0×10^{-4} M of APTSC after 70 minutes. This plot demonstrates that in the presence of APTSC, the corrosion rate of carbon steel decays significantly.

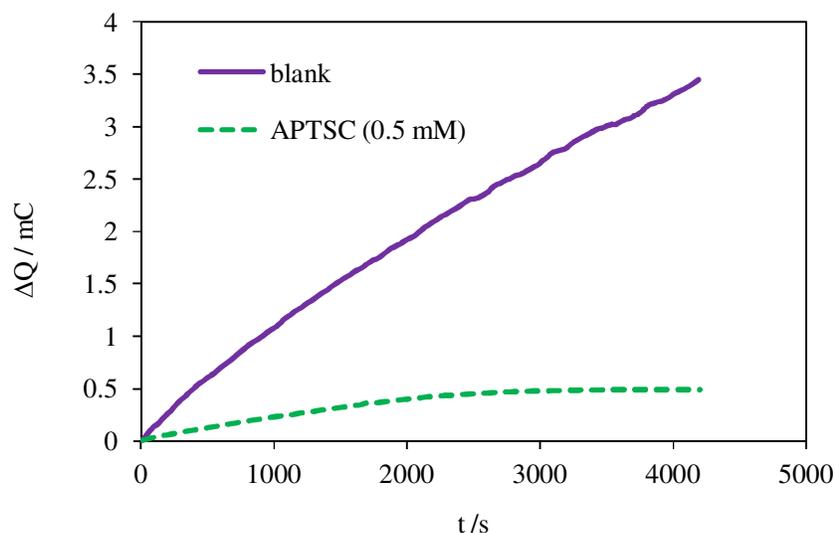


Fig. 6. Plot of total charge loaded by the steel electrode (ΔQ) vs. time in the blank solution and the solution containing 5.0×10^{-4} M of APTSC

3.4. Mechanism of inhibition

Mixed-type inhibitors block the reaction sites of the steel surface where the inhibitor molecules are adsorbed. Therefore, the active surface of the metal is suppressed and the anodic and cathodic current densities of the corrosion reaction would be decreased. In order to understand the mechanism of adsorption of the inhibitor molecules on the steel surface, first we explain the anodic dissolution of iron and the cathodic evolution of hydrogen in hydrochloric acid solution. The anodic and cathodic processes can be described as below [36-38]:



It is well known that the adsorption process on the electrode surface could be a chemisorptive or physisorptive reaction. It should be noted that in acidic solutions, both the neutral molecules and the cationic (protonated) forms of inhibitors can exist [39,40]. The physical adsorption occurs by the electrostatic interaction between the positive charge of protonated molecules and the negative charge of the steel surface (produced by the $[\text{FeCl}]_{\text{ads}}$ species). The protonated forms of inhibitor also compete with H^+ ions toward the adsorption on cathodic sites of the steel. The interaction between vacant orbitals of Fe and unshared electrons on N, O and S in the inhibitor molecules causes the chemisorption process. This type of adsorption can also occur via the pi-pi interaction between π -orbitals of the APTSC and d-electrons of the metal, which may occur after desorption of the physically adsorbed protonated species [26,41,42].

4. CONCLUSION

This paper describes application of N1-phenyl-1,2-hydrazinedicarbothioamide (TA) as a corrosion inhibitor for carbon steel in 1.0 M HCl solution. Also, FFTCCV method was used as new method for investigation of the adsorption behavior of the inhibitor. Potentiodynamic polarization and EIS results show that APTSC reduce the rate of carbon steel corrosion in acidic media. Tafel curves represent that APTSC acts as a mixed-type inhibitor suggesting its physically/chemically adsorption on the steel surface. EIS results indicate that the polarization resistance of the carbon steel surface increased with increasing the inhibitor concentration. Indeed, FFTCCV and real-time coulometric analysis at selected potentials indicates that the adsorption of APTSC takes place at about 3400 s at the beginning of the experiment and after that, the change in corrosion current maximum remains almost constant.

Acknowledgements

The authors express their appreciation to the University of Tehran Research Council for financial support of this work.

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