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REVIEW ARTICLE

Corrosion inhibition of steel in molar HCl by triphenyltin2–thiophene carboxylate

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Abstract The effect of triphenyltin2–thiophene carboxylate (TTC) on the corrosion of steel in hydrochloric acid medium was studied using gravimetric, electrochemical polarisation and electrochemical impedance spectroscopy (EIS) measurements. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor to reach 97% at 10^{-3} M. Polarisation study shows that TTC is an efficient inhibitor and acts as a mixed-type inhibitor. EIS results indicate the increase of resistance transfer (R_T) and the decrease of double layer capacitance (C_{dl}) with TTC concentration. Triphenyltin2–thiophene carboxylate molecules lead to the formation of a protective layer on the surface of steel. The inhibitor is adsorbed on the steel surface according to Langmuir isotherm.

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Contents

1. Introduction

Undesirable scale and rust in many industrial processes are generally removed by acid solutions. To ovoid the attack of acid to the bulk metal, inhibitors are generally added. Organic compounds containing heteroatoms are commonly used to reduce the corrosion attack on steel in acidic media. These compounds adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion process (Scendo, 2007; Benabdellah et al., 2007; Pillai and Narayan, 1983; Laarej et al., 2010; Bouklah et al., 2004; Chetouani et al., 2002; Touhami et al., 2000). The efficiency of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pair present the π-orbital character of free electrons and the electron density around heteroatom. The introduction of sulphur atom in heterocyclic compounds such thiophenes, has proved very good for inhibition of metal corrosion in acidic solutions (Donnelly et al., 1978; Brandt et al., 1970; Chetouani et al., 2003; Bouklah et al., 2004, 2005; Ouchrif et al., 2003). The encouraging results were obtained by bis [2-thiophene carboxylate] di-*n*-butyl tin (Ouchrif et al., 2003) and triphenyltin2–thiophene carboxylate (Benabdellah et al., 2006) on steel corrosion in sulphuric acid (96% at 10^{-3} M) and phosphoric acid (91% at 10^{-3} M). Triphenyltin compounds called also organotin compounds have a wide range of industrial applications. These compounds are effective against almost the same range of fungi as the cooper fungicides. They are also recommended for the control of the leaf spot on sugar beet and celery, blast on rice, berry disease on coffee and for algal control on paddy rice (Poller, 1970; Bollo et al., 2006; Horiguchi et al., 2006).

The objective of this work is to study the effect of triphenyltin2–thiophene carboxylate as corrosion inhibitor for dissolution of steel in molar HCl solutions using weight loss and electrochemical (polarisation and impedance) measurements.

2. Experimental parts

Triphenyltin2–thiophene carboxylate (TTC) is synthesised as described elsewhere (Benabdellah et al., 2006). Its molecular structure is shown in Fig. 1. Steel samples of following percentages 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S and the remainder iron were used. Prior to all measurements, the steel samples are abraded with a series of emery paper from 400 to 1200 grade. The specimens are washed thoroughly with bidistilled water degreased and dried with acetone.

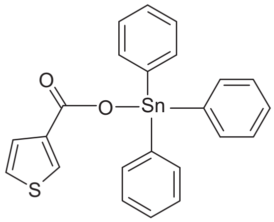

Figure 1 Molecular structure of thiophenic compound studied.

The aggressive solution (1 M HCl) is prepared by dilution of analytical grade 37% HCl with double distilled water. Triplicate experiences were made to ensure the reproducibility.

Weight loss of rectangular steel specimens of size 2 cm × 2 cm × 0.1 cm in triplicate immersed in 100 ml of electrolyte with and without the addition of different concentrations of inhibitor was determined after 6 h at 308 K.

Electrochemical measurements are carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) had the form of a disc cut form steel sheet. The exposed area to the corrosive solution is 1 cm^2. A saturated calomel electrode (SCE) and a platinum electrode are used, respectively, as reference and auxiliary electrodes. Running on an IBM compatible personal computer, the 352 Soft Corr™ III Software communicates with EG&G Instruments potentiostat–galvanostat model 263A at a scan rate of 20 mV/min. Before recording the polarisation curves, WE is first immersed into the test solution for 30 min to attain its free corrosion potential. The steel electrode is pre-polarized at −800 mV for 10 min. The polarisation curves are obtained from −800 mV to more positive values. The test solution is de-aerated with pure nitrogen. Gas bubbling is maintained through the experiments. All potentials are given in the SCE scale. The cell is thermostated at 308 ± 0.5 K.

Electrochemical impedance spectroscopy (EIS) was carried out with a Tacussel electrochemical system at E_{corr} after immersion in solution without bubbling, the circular surface of steel exposing of 1 cm^2 to the solution were used as working electrode. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. The impedance diagrams are given in the Nyquist representation.

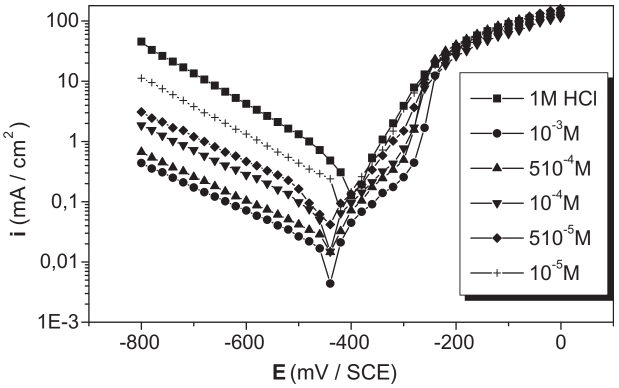

Figure 2 Polarisation curves for steel at various concentrations of TTC in de-aerated 1 M HCl.

Table 1 Electrochemical parameters and the corresponding inhibition efficiency of TTC.

TTC (M)	E_{corr} (mV/SCE)	β_c (mV/dec)	I_{corr} (μA/cm^2)	E (%)
0	−415	198	508	–
10^{-6}	−422	204	331	35
10^{-5}	−437	211	239	53
5×10^{-5}	−435	248	120	76
10^{-4}	−444	246	71	86
5×10^{-4}	−448	251	28	94
10^{-3}	−446	252	17	97

Table 2 Steel weight loss data and inhibitor efficiency of TTC at 308 K.

Inhibitor (M)	W (mg/cm^2 h)	E_w (%)	θ
Blank	1.15	–	–
10^{-6}	0.715	38	0.38
10^{-5}	0.561	51	0.51
5×10^{-5}	0.378	67	0.67
10^{-4}	0.148	87	0.87
5×10^{-4}	0.077	93	0.93
10^{-3}	0.047	96	0.96

3. Results and discussion

3.1. Polarisation measurements

Fig. 2 collects the cathodic and anodic polarisation curves of steel in molar HCl in the presence and absence of different concentrations of TTC. The corresponding electrochemical parameters values of corrosion potentials E_{corr}, corrosion current I_{corr}, cathodic Tafel slope b_c and inhibition efficiencies E% for different concentrations of TTC are summarised in Table 1. The inhibition efficiency is calculated as follows:

$$E_I\% = \left(1 - \frac{I_{corr}}{I^{\circ}_{corr}}\right) \times 100 \tag{1}$$

where I_{corr} and I°_{corr} are the corrosion current density values with and without inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

The addition of inhibitor leads to a decrease of corrosion current density (I_{corr}) which attains the lowest value (17 μA cm^{-2}) at 10^{-3} M. The higher efficiency obtained is 97%. The increase in cathodic Tafel slope with the inhibitor concentration indicates that the addition of inhibitor changes the mechanism of the hydrogen reduction. Same results were obtained in thiophene carboxylate] tin derivatives in sulphuric and phosphoric acids (Ouchrif et al., 2003; Benabdellah et al., 2006). The anodic curves of steel in 1 M HCl in the presence of TTC show that the tested compound decreases also the anodic current densities. The presence of TTC displaces E_{corr} towards more negative potentials. This result shows that TTC influences both cathodic and anodic branches and then it may be classified as a mixed type inhibitor.

3.2. Weight loss measurements

Table 2 summarizes the gravimetric trends of the steel immersed for 6 h in aerated molar HCl in the absence and the presence of the inhibitor at various concentrations at 308 K. The inhibition efficiency (E_w%) was calculated by the following relation:

$$E_w\% = \left(1 - \frac{W_{corr}}{W^{\circ}_{corr}}\right) \times 100 \tag{2}$$

W_{corr} and W°_{corr} are the corrosion rates of steel with and without inhibitor, respectively.

The addition of TTC in hydrochloric acid decreases the corrosion rate of steel. The corrosion rate attains the minimum at 10^{-3} M. The decrease of corrosion rate may be interpreted by

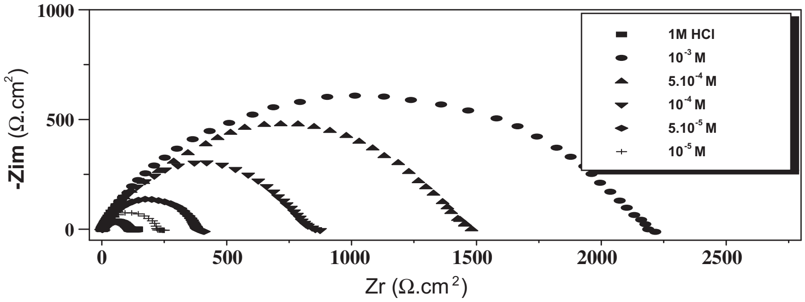

Figure 3 EIS diagrams obtained in the presence and absence of TTC at various concentrations.

the simultaneous action of inhibitor on cathodic and anodic reactions. $E\%$ increases with the TTC concentration to attain 96% at 10^{-3} M. Then the thiophene compound studied is a very efficient inhibitor of steel in the acid solution. This high inhibitory effect may be interpreted by the presence of heteroatoms (O, S) in the molecular structure of the thiophene tested. The sulphur atom with a higher electron density compared to O atom and then increases the adsorption of inhibitor on the metal surface. Moreover, in acidic solutions, thiophene ring is protonated and passes to its cationic form (Szklarska-Smialowska and Kaminski, 1973). This charge facilitates the physical adsorption which is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution.

3.3. EIS measurements

The electrochemical impedance measurements were carried out at open circuit potential (E_{corr}). Fig. 3 shows the EIS diagrams obtained as Nyquist plots in the absence and presence of different concentrations of TTC after 30 min prior to the measurements. Table 3 summarised the parameters associated with the impedance diagrams.

The obtained diagrams are not perfect semicircles, generally attributed to the frequency dispersion. The impedance diagrams obtained with molar HCl solution present one capacitive loop. The diameter of this capacitive loop increases with increasing concentration and then the resistance of transfer R_T (diameters of high frequencies loop) increases with the inhibitor concentration contrary to the decrease of the capacity of double layer which is defined as:

$$C = (2\pi f_{max} R_T)^{-1} \tag{3}$$

Table 3 Impedance parameters of steel in acid at various concentrations of TTC.

Concentration (M)	R_T (Ω cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	E (%)
0	106.9	15.82	94.1	–
10^{-6}	176.4	10	90.2	37
10^{-5}	217.3	8.92	82.1	51
5×10^{-5}	380.4	5.61	74.6	72
10^{-4}	796.6	3.16	63.2	87
5×10^{-4}	1455.8	1.78	61.4	93
10^{-3}	2135.4	1.25	59.6	95

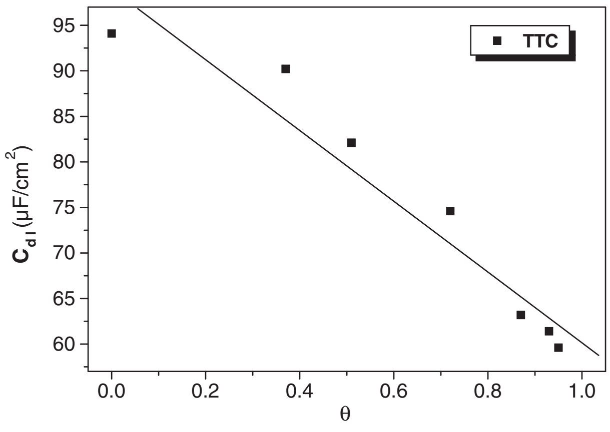

Figure 4 Variation of C_{dl} versus surface coverage θ.

The inhibition efficiencies obtained from the EIS measurements are calculated by the relation:

$$E\% = \left(1 - \frac{R_T}{R'_T}\right) \times 100 \tag{4}$$

where R_T and R'_T are the transfer resistance without and with the inhibitor, respectively.

The analysis of the EIS parameters shows that the R_T when the TTC concentration increases, giving consequently a decrease in the corrosion rate. It is important to emphasize that the values of C_{dl} decrease with increasing concentration of inhibitors for a same immersion time. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of TTC on the steel decreases its electrical capacity because they displace the water molecules and others ions originally adsorbed on the surface. This decrease may be due to the adsorption of the inhibitor on the metal surface leading to a film formation on the steel surface (Martinez and Stern, 2002). The decrease of the double layer capacitance C_{dl} may be discussed using the following relation:

$$C_{dl} = \frac{\varepsilon_0 \varepsilon}{\delta} S \tag{5}$$

where δ is the thickness of the deposit, S is the surface of the electrode, ε_0 is the permittivity of the air and ε is the medium dielectric constant.

The relation shows that the decrease in C_{dl} values (Fig. 4) may be due to a decrease of local dielectric constant ε (McCafferty and Hackerman, 1972) or by an increase of the thickness of the adsorbate layer of inhibitor at the metal surface (Bastidas et al., 2000).

The different values of $E\%$ obtained from EIS, polarisation and gravimetric methods are in good agreement.

3.4. Adsorption isotherm

Additional information about the properties of the tested compound may be provided from the kind of adsorption isotherm. Several adsorption isotherms were tested and the Langmuir adsorption isotherm was found to provide best description of the adsorption behaviour of the investigated inhibitor. The Langmuir isotherm is given by the equation (Langmuir, 1947):

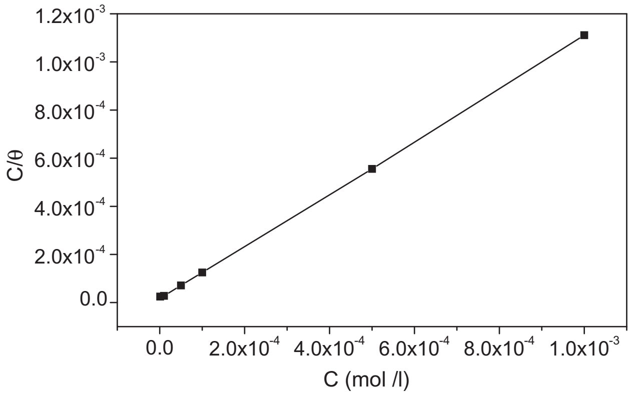

Figure 5 Langmuir isotherm adsorption of TTC on steel in 1 M HCl.

$$\frac{C}{\theta} = \frac{1}{k} + C \tag{6}$$

$$k = \frac{1}{55.5} \exp\left(-\frac{\Delta G^{\circ}_{\mathrm{ads}}}{RT}\right) \tag{7}$$

where C is TTC concentration, θ the fraction of the surface covered determined by E/100, k the adsorption equilibrium constant and $\Delta G^{\circ}_{\mathrm{ads}}$ the standard free energy of adsorption reaction.

The plot of C/θ versus C gives a straight line as shown in Fig. 5. The linear regression coefficient values $R = 0.9996$ is very close to 1. The slope is 1.091 to close to unity, confirming that the adsorption of TTC in 1 M HCl obeys the Langmuir adsorption isotherm. The equilibrium constant of the adsorption process, k, calculated from the intercept of the straight line gives 56818.4. This result leads to evaluating $\Delta G^{\circ} = -38.3$ kJ/mol. The value of ΔG_{ads} is too negative indicating that TTC is strongly adsorbed on the steel surface (Popova et al., 2003; Ousslim et al., 2009; Tebbji et al., 2007).

4. Conclusion

- Inhibitor tested is an efficient inhibitor for steel corrosion in 1 M HCl.
- Polarisation measurements show that TTC acts as a mixed type inhibitor. The inhibition efficiency increases with the increase of concentration to reach 97%.
- The inhibitor efficiencies determined by EIS, by polarisation and by gravimetric methods are in good agreement.
- The adsorption of TTC on the steel surface obeys to the Langmuir isotherm model.

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