

Inhibiting properties and adsorption of some thioamides on mild steel in sulphuric acid solutions

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Received: 8 June 2007 / Revised: 18 April 2008 / Accepted: 21 April 2008 / Published online: 14 May 2008
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Abstract The inhibiting properties and adsorption behaviour of thioacetamide (TAA), thiobenzamide (TBA) and thiocinnamamide (TCA) on mild steel in sulphuric acid solution were studied by gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. TBA and TCA were found to be mixed type inhibitors providing good corrosion inhibition. Different mechanisms of adsorption and corrosion inhibition were observed for the tested thioamides. In the cases of TBA and TCA, the adsorption of the compounds is chemical and the values of the activation energy (E_a) and the pre-exponential factor (A) are lower than the corresponding values observed in inhibitor free solution. The adsorption of TAA is physical and the values of E_a and A are higher than the corresponding values in sulphuric acid solution. The adsorption process of TBA and TCA on the

mild steel/sulphuric acid solution interface is described by Langmuir's isotherm. A correlation between the adsorption capability and the inhibiting efficiency of the molecules and their donor–acceptor properties (E_{HOMO} and E_{LUMO}) has been established. It is ascertained that the protection effect of TAA depends on the amount of hydrolysis products.

Keywords Corrosion inhibition · Adsorption · Thioamides · Mild steel · Sulphuric acid

1 Introduction

The inhibition of corrosion by organic compounds is usually related to their adsorption on the metal surface [1–18]. The adsorption process depends on different factors such as the nature and the charge of the metal surface, the temperature and pH of the corrosion media and the molecular structure of the organic compounds (type of functional groups, steric factor and the electron density distribution).

For numerous series of organic compounds molecular orbital calculations have been used to correlate structural and electronic parameters of the inhibitor molecules with their adsorption behaviour and therefore with the inhibition efficiency [10–29].

The aim of the present work is to study the adsorption behaviour and inhibiting properties of thioacetamide (TAA), thiobenzamide (TBA) and thiocinnamamide (TCA) on mild steel in sulphuric acid solutions, as well as to obtain the correlation between inhibitor performance, respectively adsorption capability of TAA, TBA and TCA and their chemical structure. TAA and TBA have been studied as inhibitors of mild steel corrosion in hydrochloric [26–28, 30] and in sulphuric acid solutions [29], but the

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correlation between the inhibition efficiency and molecular structure of the compounds is discussed in the cited works without taking into account the protonation of thioamides in acid solutions [31]. However, it was ascertained [12, 13] that the protonation of organic molecules in acidic solutions generally produces a considerable change in the partial charges distributed at the adsorption centres of the molecules as well as in the values of the energy of the highest occupied molecular orbital (E_{HOMO}) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}), which generally relate to the donor–acceptor properties of organic molecules. Another neglected problem in studying inhibition properties of TAA is the hydrolysis of compound in acidic aqueous solutions [2, 32]. The compound is relatively stable at 20 °C, but at higher temperature the rate of TAA hydrolysis significantly increases [32].

The inhibiting properties of the selected thioamides have been estimated by the use of gravimetric measurements, potentiodynamic polarization technique and electrochemical impedance spectroscopy.

2 Experimental details

Quantum-chemical calculations were carried out using of the AM1 method [33–35]. The partial charges of the atoms in the molecules, the energies: E_{HOMO} and E_{LUMO} , as well as the length of valence bonds and the dihedral torsion angles were calculated.

The experiments were conducted in 0.1 M H_2SO_4 solutions, containing different concentrations of the organic substances: thioacetamide (TAA), thiobenzamide (TBA) and thiocinnamamide (TCA). The compounds were added to the corrosive medium as ethanol solutions with the aim of increasing their solubility. The concentration of ethanol was 2 vol.% and was maintained constant for all solutions. The solutions were prepared with doubly distilled water and A.R. grade chemicals.

Mild steel samples (C-0.039, Mn-0.38, Cu-1.112, Ni-0.07, Si-0.003, S-0.02, P-0.22%) of $4.0 \times 5.0 \times 0.25$ cm were used for weight loss experiments. The samples were polished mechanically with abrasive paper (N:240 to N:900) degreased with acetone and rinsed with ethanol. The electrochemical experiments were performed in a conventional three-electrode glass cell with working volume of 100 mL. A working electrode was a cylinder embedded in a Teflon holder. The surface area exposed to the electrolyte was 0.5 cm^2 . Before experiments the electrode surface was polished mechanically and treated in the same way as described above. A Pt counter electrode and a saturated calomel electrode as reference electrode were used. All potential values are referred to the normal hydrogen electrode.

The measurements were carried out by a Solartron 1286/1250 system. The potentiodynamic polarisation curves were recorded at a sweep rate of 1 mV s^{-1} after the steady-state potential had been established in cathodic or anodic direction.

The impedance measurements were performed using an ac signal with amplitude 5 mV in the frequency range from 65 kHz to 0.01 Hz. The spectra were recorded under open-circuit conditions after 1 h exposure in the test solution.

3 Results and discussion

3.1 Quantum chemical calculations

Molecular orbital calculations were performed for the molecules of thioacetamide (TAA), thiobenzamide (TBA) and thiocinnamamide (TCA). In addition, calculations of the protonated forms of the molecules were carried out because in acid medium the thioamides are protonated [31] due to the presence of the free electron pairs on sulphur and nitrogen atoms. The hydrogen cation from the solution can be bonded to the S atom as well as to the N atom in the molecules of TAA, TBA and TCA. The data obtained by quantum chemical calculations show that the protonation is realized at the S atom of the compounds. The values of the distribution of partial charges in the molecules and their protonated forms are presented in Fig. 1a and b respectively. It is ascertained that the protonation produces a noticeable change of the partial charges distributed at the adsorption centers: S atom, amino and methyl groups and phenyl radicals. In Table 1, the values of electron density at S and N atoms of the protonated forms as well as of E_{HOMO} and E_{LUMO} for molecules in non-protonated and protonated form are summarized. The comparison of quantum chemical calculation results shows that protonation produces a considerable change of E_{HOMO} and E_{LUMO} values. The non-protonated molecules of thioamides have similar values for energy of the highest occupied molecular orbital (E_{HOMO}) while for protonated forms the E_{HOMO} values differ significantly and increase in the order $\text{TAA} < \text{TBA} < \text{TCA}$. The essential difference in E_{LUMO} values was established for the molecules of tested thioamides and their protonated forms. The E_{LUMO} values for protonated forms increase in inverse order than these for non-protonated forms. These results demonstrate that in acid medium, the values of E_{HOMO} and E_{LUMO} for protonated molecules have to be used for correlation of the inhibition efficiency and the chemical structure of thioamides.

3.2 Weight loss measurements

The inhibition efficiency of the selected thioamides on mild steel corrosion was examined by weight loss measurements.

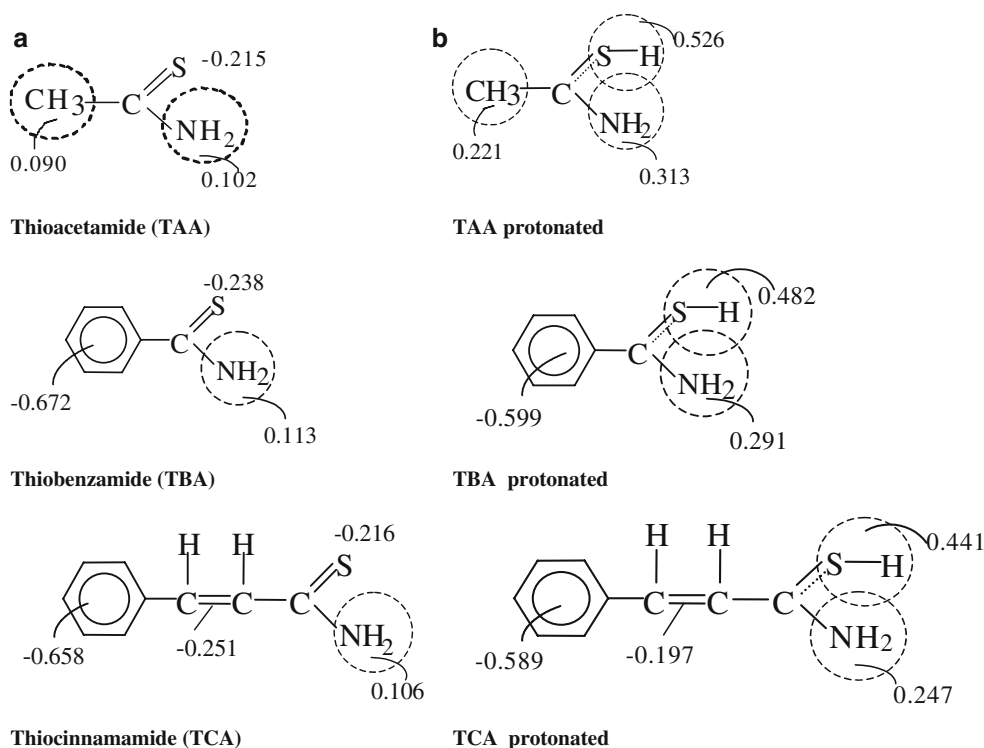


Fig. 1 Molecular structure and distribution of partial charges (a) in the molecules of the tested thioamides; (b) in the protonated form of thioamides

Table 1 Data from quantum chemical calculation for tested thioamides

Compound	E_{HOMO} (eV)		E_{LUMO} (eV)		Electron density for protonated form	
	Neutral molecule	Protonated form	Neutral molecule	Protonad form	At N atom	At S atom
TAA	-8.498	-15.263	-0.122	-6.046	5.244	5.496
TBA	-8.515	-13.701	-0.808	-5.758	5.257	5.534
TCA	-8.512	-12.640	-1.034	-5.720	5.285	5.581

The influence of inhibitor concentration and temperature was investigated. The inhibition efficiency, IE_w (%), for each concentration of the tested thioamides was determined from weight loss data by the following equation:

$$IE_w = r_o - r / r_o \cdot 100 \quad (1)$$

where r_o and r are the average corrosion rates ($\text{g m}^{-2} \text{h}^{-1}$) of mild steel in sulphuric acid solution in the absence and presence of inhibitors, respectively.

The dependence of the inhibition efficiency on the concentration of the compounds in 0.1 M H_2SO_4 at 20 °C is presented in Fig. 2. It is evident that the inhibition efficiency increases with the increase of thioamides concentration. Maximum inhibition for TCA is reached at relatively low concentration of 0.1 mM, which corresponds to the maximum solubility of the substance at these conditions. For TAA and TBA the maximum protective effect was obtained at a concentration of 1 mM.

The comparison of the values of IE_w (%) at a concentration of 0.1 mM shows that the inhibition efficiency increases in the order $\text{TAA} < \text{TBA} < \text{TCA}$. The data in Table 1 show that E_{HOMO} and E_{LUMO} , as well as the electron density of S and N atoms in the protonated form of the compounds increase in the same order. This clearly indicates a dependence of the inhibition efficiency on the molecular structure parameters.

The influence of temperature on the inhibition efficiency was studied at different concentrations of selected thioamides. The dependences IE_w (%) on temperature at a concentration of 0.1 mM are presented in Fig. 3. The results show that the inhibition efficiency of TBA and TCA increases with increase of temperature. This indicates that the corrosion inhibition with TBA and TCA is a result of the chemical adsorption of the compounds. In contrast, in the case of TAA the inhibition efficiency decreases with increase in temperature, probably as a

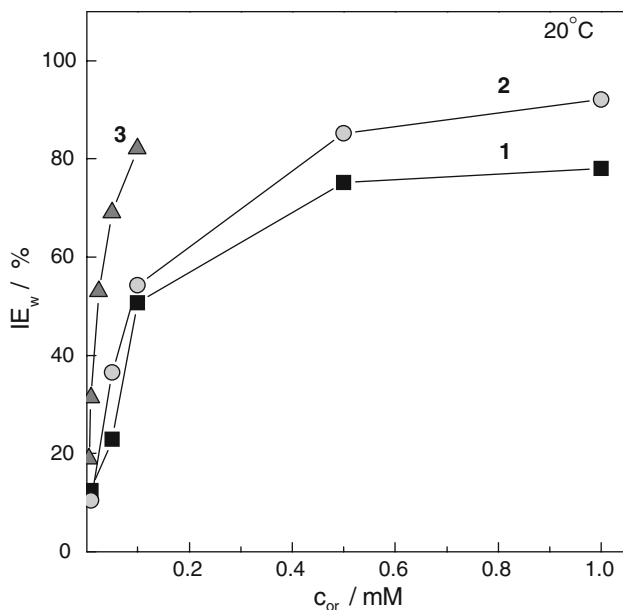


Fig. 2 Dependence of the inhibition efficiency IE_w (%) on the concentration of the compounds c_{or} (mM) for mild steel corrosion in 0.1 M H_2SO_4 at 20 °C in presence of (1) TAA (2) TBA and (3) TCA

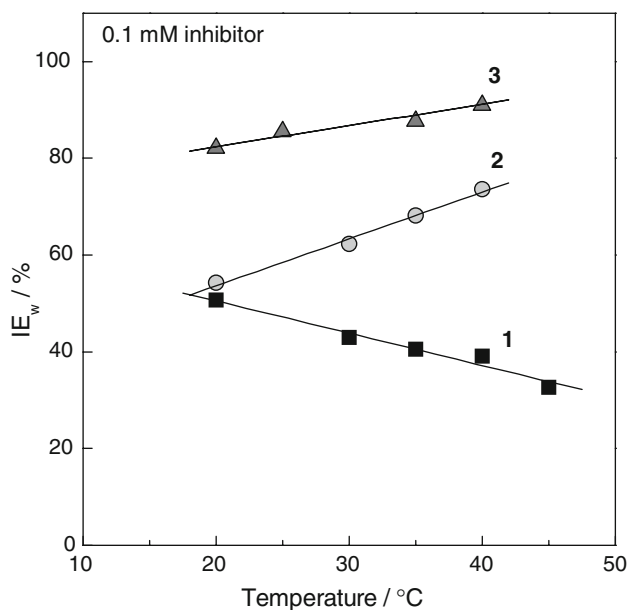


Fig. 3 Inhibition efficiency at 0.1 mM concentration of compounds against temperature: (1) TAA (2) TBA and (3) TCA

result of desorption, characterizing the physical adsorption.

The effect of temperature on the corrosion rate (r) at different concentrations of TAA, TBA and TCA is shown in Fig. 4 (Arrhenius plots). It is evident that the corrosion rate increases with increase in temperature, both for the blank and for the inhibited solutions. Figure. 4b and c show

that at higher concentrations TBA and TCA significantly slow down the corrosion rate within the entire temperature range. The apparent activation energy (E_a) and the pre-exponential factor (A) from the Arrhenius equation ($r = A e^{-E_a/RT}$) were determined from the slopes and the intercepts respectively of the straight lines in Fig. 4 and are presented in Table 2.

Summarizing the results obtained for E_a and A in sulphuric acid solutions with and without the addition of thioamides at various concentrations, it can be concluded that the mechanism of corrosion inhibition differs in the presence of selected thioamides. In sulphuric acid solution containing TBA and TCA, the E_a and A values are lower than those in the uninhibited solution. With increase in TBA and TCA concentrations the E_a and A values decrease. For TAA the values of E_a and A are higher than those for blank acid solution. In this case however, with increase of TAA concentration both values of E_a and A increase.

3.3 Adsorption isotherms

The adsorption isotherms provide specific information about the adsorption behaviour of the inhibitors i.e. the interaction between the adsorbed molecules and metal surface as well as adsorbate/adsorbate interactions in the adsorption layer. The degree of surface coverage (θ) for different concentrations of the inhibitors in sulphuric acid solution was evaluated using the inhibition efficiency data ($\theta = IE_w/100$). Different adsorption isotherms were tested for agreement with the experimental data.

The linear relations in the $\ln[\theta/(1 - \theta)]$ on $\ln c_{or}$ plots for TBA and TCA at all examined temperatures (Fig. 5a and b) suggest that the adsorption of these compounds on mild steel surface follows the Langmuir adsorption isotherm:

$$Bc_{or} = [\theta/(1 - \theta)] \quad (2)$$

where B is the equilibrium constant of the adsorption process. The validity of Langmuir's isotherm of TBA and TCA adsorption on mild steel indicates that the interaction forces between the molecules in the adsorbed layer are equal to zero. Higher values of the equilibrium constant (B) were obtained for TCA for all temperatures (Table 3). This confirms that the adsorption capability of TBA and TCA depends on their donor-acceptor properties (E_{HOMO} and E_{LUMO} values).

The degree of surface coverage (θ) estimated at different concentrations of TAA were tested graphically as to whether they fitted the Langmuir, Frumkin, Temkin and Flory-Huggins adsorption isotherms. However, the correlation coefficient R between θ and c_{or} for all adsorption isotherms was below 0.65. The adsorption of TAA on the

Fig. 4 Temperature dependence of mild steel corrosion in 0.1 M H₂SO₄ (Arrhenius plots) in the presence of: (a) TAA: (1) 0, (2) 0.05, (3) 0.1 and (4) 1 mM; (b) TBA : (1) 0, (2) 0.01, (3) 0.05, (4) 0.1 and (5) 1 mM and (c) TCA: (1) 0, (2) 0.01, (3) 0.025, (4) 0.05, and (5) 0.1 mM

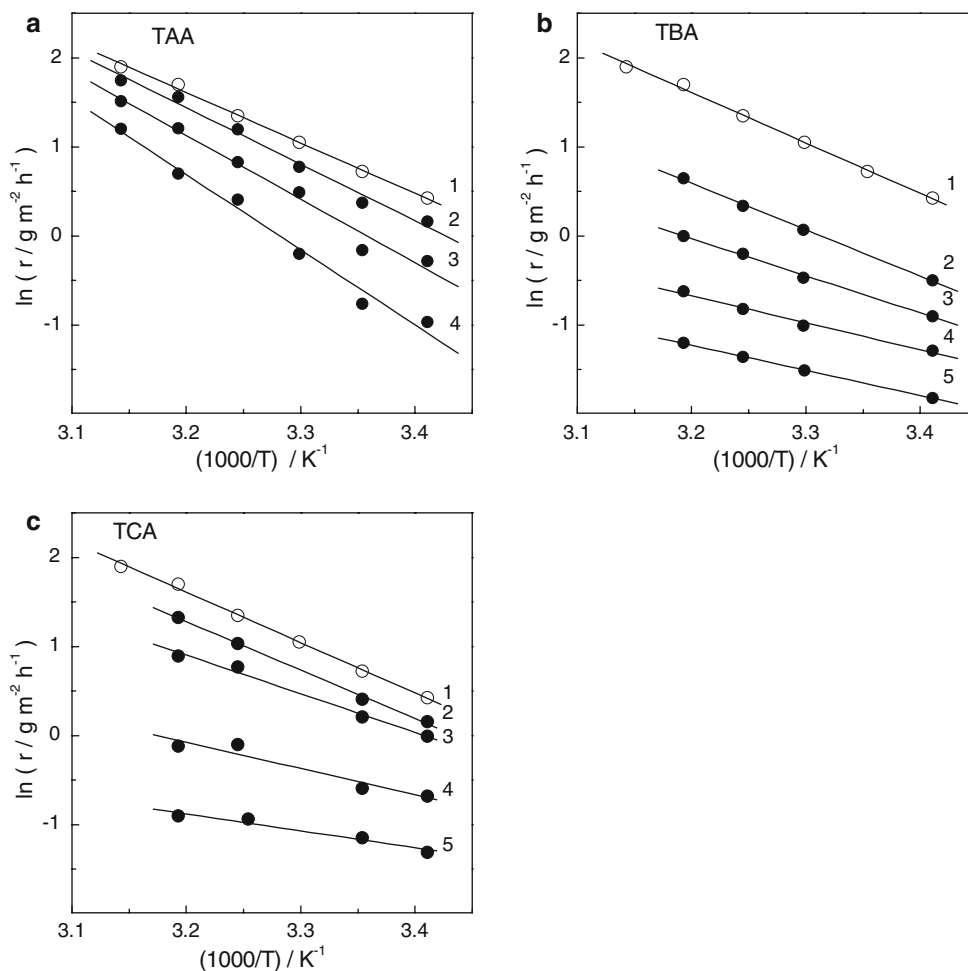


Table 2 Apparent activation energy (*E_a*) and the pre-exponential factor (*A*) for tested thioamides at different concentrations obtained by weight loss measurements

Compound	Concentration (mM)	<i>E_a</i> (kJ mol ⁻¹)	<i>A</i> (h ⁻¹)
Blank	–	47.06	3.68 × 10 ⁸
TAA	0.05	52.76	2.78 × 10 ⁹
	0.10	59.43	2.65 × 10 ¹⁰
	0.50	73.59	4.78 × 10 ¹²
	1.00	74.55	5.76 × 10 ¹²
TBA	0.05	43.36	2.99 × 10 ⁷
	0.10	34.65	6.00 × 10 ⁵
	0.50	25.22	8.39 × 10 ³
	1.00	23.50	2.48 × 10 ³
TCA	0.005	45.19	1.28 × 10 ⁸
	0.01	36.15	2.73 × 10 ⁶
	0.05	21.97	4.13 × 10 ³
	0.10	16.39	2.81 × 10 ²

mild steel/sulphuric acid solution interface can therefore be considered as a non equilibrium process due to the TAA hydrolysis [2, 32].

3.4 Electrochemical impedance measurements

The impedance spectra of mild steel in 0.1 M H₂SO₄ solutions without and with addition of the tested inhibitors after 1 h of exposure at 20 °C are shown as Nyquist plots in Fig. 6. The concentration of 0.1 mM was selected to compare the effect of compounds since it corresponds to the maximum solubility of TCA.

The quantitative analysis of the experimental data was performed by a nonlinear least squares minimization method [36]. The impedance spectra in the sulphuric acid solution consist of two components: a high-frequency capacitive semicircle and a low-frequency inductive loop. The equivalent circuit describing the processes on the mild steel/solution interface is shown in Fig. 6a, where *R_t* is the charge transfer resistance and *C_{dl}* is the double-layer capacitance. The resistor *R* and the inductance *L* are elements associated with the relaxation of the adsorbed intermediates. In the presence of TAA the character of the spectrum is similar to that of an inhibitor free solution, and no significant changes in the diameter of the high-frequency semicircle associated with the charge transfer resistance *R_t* is visible. In the presence of TBA and TCA

Fig. 5 Dependence of $\ln[\theta/(1-\theta)]$ on $\ln c_{or}$ (Langmuir's adsorption isotherm) for (a) TBA at (1) 20, (2) 30, (3) 35 and (4) 40 °C and (b) TCA at (1) 20, (2) 25, (3) 35 and (4) 40 °C

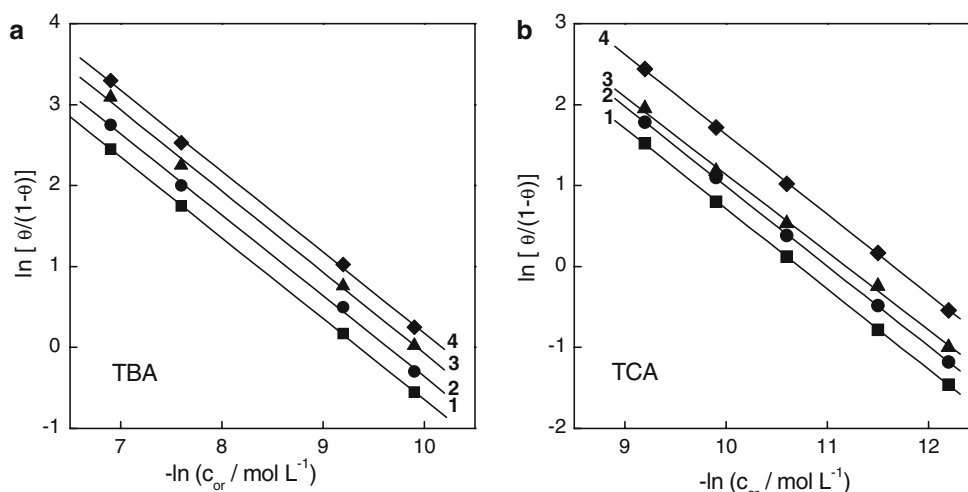


Table 3 Values of the equilibrium constant (B) for TBA and TCA obtained by weight loss measurements

Temperature (°C)	$10^{-4} B$ (mol L $^{-1}$)	
	TBA	TCA
20	1.17	4.15
25	1.38	5.18
30	1.55	6.11
35	2.11	7.31
40	2.32	8.93
45	2.69	10.48

(Fig. 6b) the diameter of the high-frequency semicircle increases and the low-frequency inductive loop disappears. This result indicates different mechanism of adsorption of TBA and TCA on the mild steel surface.

The calculated values of the corresponding parameters of the equivalent circuits in the absence and presence of the investigated compounds in the corrosive medium are summarized in Table 4. The significant increase of R_t and

the decrease of C_{dl} is clear evidence of the inhibitor properties of TBA and TCA at concentration of 0.1 mM.

3.5 Polarization measurements

The inhibiting effect of selected thioamide compounds on the partial corrosion reactions of mild steel was investigated by use of the potentiodynamic polarisation technique. Figure 7 shows polarization curves recorded after 1 h of exposure in 0.1 M H $_2$ SO $_4$ solution without and with addition of different concentrations of thioamides tested at 20 °C.

Table 4 Impedance parameters for mild steel in 0.1 M H $_2$ SO $_4$ solution without and with 0.1 mM of tested thiamides

Compound	R_t (Ω cm 2)	C_{dl} (μ F cm $^{-2}$)	L (H cm 2)	R (Ω cm 2)
Blank	117	83.6	89	706
TAA	121	74.6	140	839
TBA	570	26.3	–	–
TCA	952	19.4	–	–

Fig. 6 Electrochemical impedance diagrams for mild steel in 0.1 M H $_2$ SO $_4$ solution without and with 0.1 mM of tested inhibitors after 1 h exposure in solution

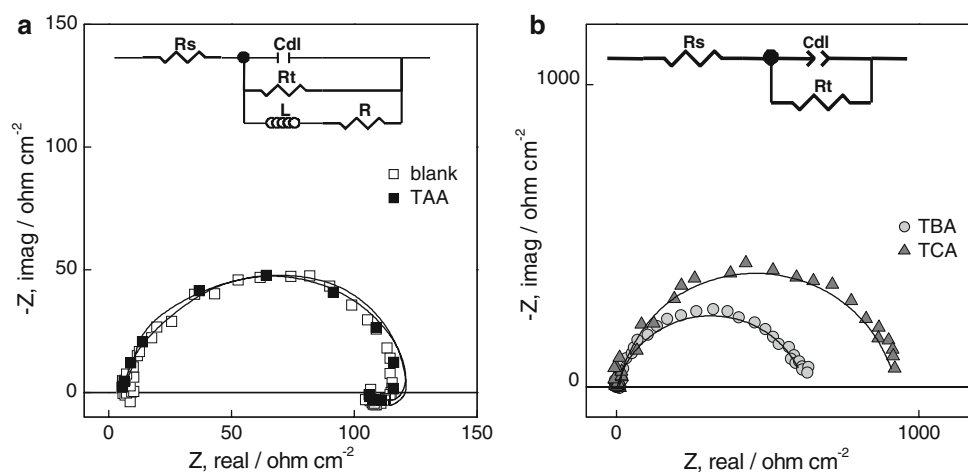
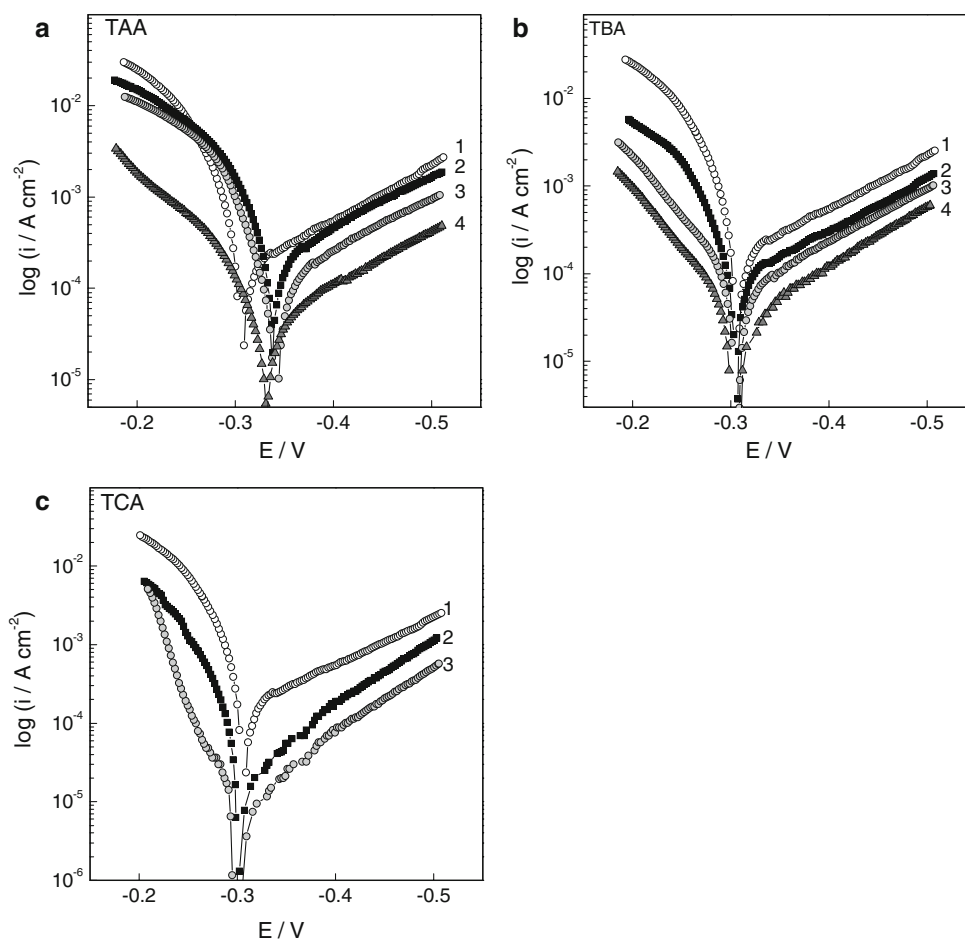


Fig. 7 Potentiodynamic polarization curves of mild steel electrode in 0.1 M H₂SO₄ (curve 1) and in the presence of (a) TAA: (2) 0.1, (3) 1 and (4) 10 mM; (b) TBA: (2) 0.01, (3) 0.1 and (4) 1 mM and (c) TCA: (2) 0.01 and (3) 0.1 mM



The inhibition efficiency was calculated using the equation:

$$IE(\%) = (I_{\text{corr},0} - I_{\text{corr}}) / I_{\text{corr},0} \quad (3)$$

where $I_{\text{corr},0}$ and I_{corr} are the corrosion current densities without and with inhibitor, respectively. These were determined by extrapolation of the Tafel lines and the open circuit potential of the corresponding polarization curves. The values of open circuit potential (E_{corr}) and corrosion current densities (I_{corr}) as well as the calculated inhibition efficiency are presented in Table 5.

The obtained polarization curves show that the TAA addition shifts the corrosion potential (E_{corr}°) in negatively. This means that TAA is an inhibitor of cathodic type. However, at the highest concentration of TAA (10 mM) significant inhibition of the anodic reaction is also observed. TBA and TCA act as inhibitors of mixed type. Their addition slows down the rate of both partial corrosion reactions without shifting the corrosion potential (E_{corr}°). The cathodic Tafel slopes do not change significantly in the presence of inhibitors. This fact suggests that these compounds do not change the kinetics of hydrogen evolution.

Table 5 Data from polarization measurements for mild steel in 0.1 M H₂SO₄ solution without and with thiamides

Compound	Concentration (mM)	E_{corr} (V)	I_{corr} (mA cm ⁻²)	IE (%)
Blank		-0.303	0.158	-
TAA	0.1	-0.338	0.174	-
	1	-0.338	0.101	36.0
	10	-0.336	0.033	79.1
TBA	0.01	-0.305	0.078	50.6
	0.1	-0.304	0.056	64.5
	1	-0.304	0.024	84.8
TCA	0.01	-0.302	0.018	88.6
	0.1	-0.300	0.009	94.3

The inhibition efficiency of thioamides increases with increase in concentration (Table 5). The relatively high IE value (about 94%) in the presence of TCA indicates good protective properties of this compound toward mild steel corrosion in acid medium.

The inhibition efficiency obtained by polarization measurements for TBA and TCA show good correlation with results obtained by gravimetric measurements at 20 °C. For

- (v) It is ascertained that the protective effect of TAA depends on the amount of hydrolysis products.

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