

N-(2-hydroxybenzilidene) thiosemicarbazide surfactant as an effective inhibitor for corrosion of carbon steel in diluted acidic solutions. Part I

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A Schiff base, namely N-(2-hydroxybenzilidene) thiosemicarbazide (HBTC) was investigated as an inhibitor for carbon steel in diluted acidic solutions (DAS) using electrochemical measurements. The morphology of the surfaces before and after corrosion was examined by scanning electron microscopy (SEM). The results showed that HBTC acts as an excellent corrosion inhibitor in DAS by suppressing simultaneously the cathodic and anodic processes *via* chemical adsorption on the surface, which followed the Langmuir adsorption isotherm. The inhibition efficiency increased with the increase HBTC concentration. The adsorption mechanism of the compound was discussed in terms of kinetic parameters deduced from the experimental data and UV-VIS spectrophotometry.

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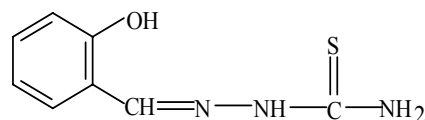
1. Introduction

In practice, numerous chemical compounds are used for the prevention and long-term control of corrosion inhibiting the aggressive action of the medium in contact with metallic constructions¹⁻⁸ and / or to improve the electro-deposition processes of the other metals on different substrates⁹. The importance of inhibition is much greater in solutions of hydrochloric acid since iron and its alloys are the most exposed materials both in industrial and other media, while these metallic materials are more susceptible to being attacked in an acid pH medium rather than in an alkaline one. The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on the metal surface under particular experimental conditions. The available results show that most inhibitors act by adsorption on the metal surface. The strength of adsorption, and hence, the extent of inhibition is dependent on the nature of the organic compounds and the nature of the metal and the corrosive media.

In the present paper, was investigated a Schiff base, namely N-(2-hydroxybenzilidene) thiosemicarbazide (HBTC) as an inhibitor for carbon steel in diluted acidic solutions (DAS) containing 0.15 M NaCl and 0.001 M HCl using electrochemical measurements. Scanning electron microscopy was also used to examine the changes of surface morphology of the steel corroded in the media without and with addition of the inhibitor. Based on the experimental data, several kinetic parameters were estimated. The adsorption mechanism of the inhibitor onto carbon steel surface in DAS is also discussed.

2. Experimental

The carbon steel used had the following composition (weight %): C=0.1%; Si=0.035%; Mn=0.4%; Cr=0.3%; Ni=0.3%, with the balance in Fe. The samples were mechanically polished with different grades of emery paper (down to 600), degreased with acetone and dried. Diluted acidic solution (DAS) containing 0.15 M NaCl and 0.001 M HCl was used as the blank corrosion test solution. The inhibitor used was a Schiff base, N-(2-hydroxybenzilidene) thiosemicarbazide (HBTC) in concentrations of 0.5 mM; 1 mM; 1.5 mM; 2 mM; it has following chemical structure:



N-(2-hydroxybenzilidene) thiosemicarbazide (HBTC) has been synthesized at Moldova State University, Chisinau – Prof.dr. Aurelian Gulea. All reagents were obtained from Fluka.

For the study of polarization, a standard corrosion cell with a working electrode made of carbon steel with an active surface of 2 cm² was used. The saturated calomel electrode (SCE) was used as a reference electrode. The auxiliary electrode was a platinum electrode (surface area - 1 cm²). The potentiodynamic polarization was conducted with a scan rate of 10 mV.s⁻¹, in an electrochemical system, VoltaLab 40, with a personal computer and VoltaMaster 4 software. The immersion time of the plates in the respective media was 30 minutes in open circuit, at room temperature.

The morphology of the steel surface before and after treatment in the above mentioned solutions was examined by scanning electron microscope (Vega Tescan).

The adsorption process of organic compounds from aqueous phase on the electrode surface was demonstrated using UV-VIS analysis reports of DAS containing 2 mM HBTC, before and after corrosion of carbon steel. In the UV-VIS spectrophotometry, a spectrophotometer of type Varian-Cary 50 (software-Cary Win UV) was used.

3. Results and discussion

3.1 Electrochemical measurements

3.1.1 Tafel polarization

Fig. 1 shows the polarization curves of carbon steel in DAS blank and in the presence of various concentrations of HBTC, at room temperature. The anodic and cathodic over potentials of the steel electrodes in DAS containing different concentrations of Schiff base are shifted to a higher value, with increasing current density. The presence of organic inhibitor in the corrosive medium increases the anodic and cathodic over potentials and shifts the corrosion potential (E_{corr}) to higher values. The increase in HBTC concentrations leads to both anodic and cathodic current inhibition, but the reduction in the anodic current was more significant than that of the cathodic current. This shows that the addition of HBTC reduces anodic dissolution and also delays the hydrogen evolution reaction. This suggests that, although inhibition is of mixed type, it is predominantly anodic. The corrosion current was calculated at intercept of the anodic and cathodic Tafel lines to corrosion potential, using VoltMaster 4 software.

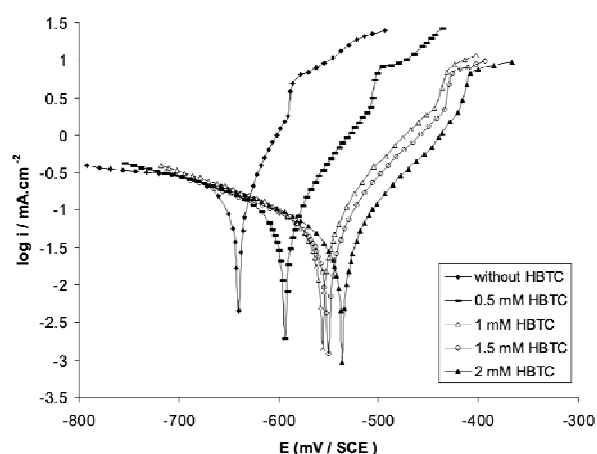


Fig. 1. Potentiodynamic curves for carbon steel corroded in DAS without and with various concentrations of HBTC inhibitor.

The results showed that the corrosion current density (i_{corr}) decreased with increasing the concentration of the HBTC, which indicates that this compound acts as

inhibitor by adsorption onto steel surface, and the degree of inhibition depends on the concentration of Schiff base. The slopes of the anodic and the cathodic Tafel lines (b_a , b_c) were slightly changed on increasing the concentration of the tested compound. The small change may be due to surface blockage by the HBTC. The percentage inhibition efficiency (IE) of Schiff base inhibitor was also determined from the polarization measurements according to the following equation:

$$IE = \frac{i'_{corr} - i_{corr}}{i_{corr}} \times 100 \quad (1)$$

i'_{corr} and i_{corr} are the corrosion current densities in solution without and with HBTC, respectively, determined by extrapolation of Tafel lines to corrosion potential. The values of inhibition efficiency increase with PVA concentration reaching a maximum value of 80.5 % at 2 mM HBTC concentration.

3.1.2 Polarization resistance method- Stern method

The polarization curves obtained in the potential ranges near to corrosion potentials were recorded with a scan rate of 10 mV s^{-1} . The linearization was accomplished in the domain of over-voltages values $\pm 10 \text{ mV}$ (Fig. 2).

The slopes $(di/dE)_{E \rightarrow E_{corr}}$ of the lines from Fig. 2, represent the polarization conductance. Polarization resistance ($R_p - k \Omega \text{ cm}^2$) was calculated using relation 2.

$$\left(\frac{di}{dE} \right)_{E \rightarrow E_{corr}} = \frac{1}{R_p} \quad (2)$$

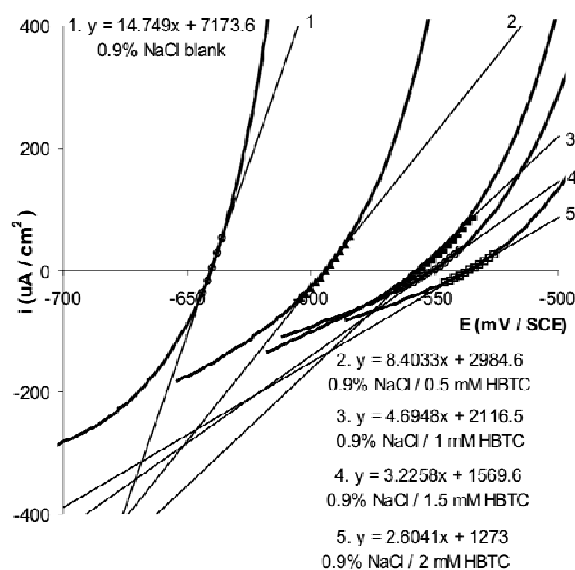


Fig. 2. Polarization resistance (R_p) of carbon steel corroded in DAS without and with various concentrations of HBTC inhibitor.

The study of the response of stainless steel material without and with HBTC given by polarizing those in DAS, shown a shift polarization resistance (R_p) to a higher values with increasing in HBTC concentration. (Fig. 2). This suggests that the inhibition of the stainless steel corrosion in the presence of HBTC occurs by adsorption at site on the metal surface.

The percentage inhibition efficiency (IE) of HBTC inhibitor was calculated according to the following equation:

$$IE = \left(1 - \frac{R_p^0}{R_p}\right) \times 100 \quad (3)$$

Table1. The effect of concentration of HBTC compound on the corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (b_a & b_c), percentage inhibition efficiency (IE) of carbon steel corroded in DAS, at room temperature.

C-HBTC	E_{corr}	i_{corr}	R_p	b_a	b_c $mV\ dec^{-1}$	IE (%)	
						From Tafel	From Stern
0	-640	239.0	67.8	68.6	-314	0	0
0.5	-594	128.3	119.0	76.4	-298	46.3	43.0
1	-556	79.1	213.0	76.8	-340	66.9	68.1
1.5	-550	58.5	310.0	77.0	-293	75.5	78.1
2	-536	46.6	384.0	78.0	-291	80.5	82.3

3.1.3 Adsorption isotherm

The adsorption of inhibitor molecules on metal surface is a substitute process, during which the adsorbed water molecules on the metal surface are replaced by inhibitor molecules. In order to get a better understanding for the adsorption mechanism, the Langmuir adsorption isotherm equation was employed as following equation:

$$\frac{\theta}{1-\theta} = K \cdot C \quad (4)$$

where θ is the degree of coverage ($\theta = EI / 100$ – from Tafel polarization), K is the equilibrium constant of the adsorption-desorption process, C is concentration of the HBTC (C-HBTC). The plots of $\theta/1-\theta$ versus C-HBTC yielded a straight line (Fig. 3); the slope of this line represents K . From Fig. 3 it can be observed that K has a high value of $2096\ M^{-1}L$.

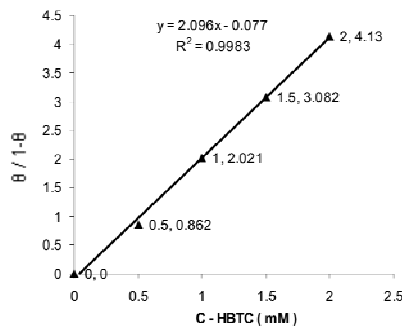


Fig. 3. The result of a Langmuir diagram in case of corrosion inhibition of carbon steel in DAS containing various concentrations of HBTC.

where R_p^0 is polarization resistance in absence of inhibitor and R_p is the polarization resistance in presence of HBTC. The values of inhibition efficiency increase with HBTC concentration reaching a maximum value of 82 % at 2 mM HBTC concentration, nearly equal with the value obtained from Tafel polarization. The numerical values of the electrochemical parameters and of the inhibition efficiency on behaviour of carbon steel in DAS blank and in DAS containing different concentrations of HBTC were calculated using VoltaMaster 4 software with an error of $\pm 1.5\%$, and are presented in Table 1.

This isotherm clearly reveals that the adsorption of the HBTC on the carbon steel surface obeys the Langmuir adsorption isotherms, and the inhibitor molecules are adsorbed on steel surface forming a film, which prevents the carbon steel from corrosion induced by the medium.

The free standard energy of adsorption ΔG_{ads}^0 was calculated with the relation 5.

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^0}{R \cdot T}\right) \quad (5)$$

where R is the universal gas constant, T is temperature (K) and 55.5 is the molar concentration of water in the solution. The value of ΔG_{ads}^0 is negative ($-28.88\ KJ \cdot mol^{-1}$), which shows that the process of adsorption is spontaneous.

3.1.4 SEM observation

The electrochemically-corroded carbon-steel samples in DAS without HBTC and in DAS containing HBTC were also tested using the SEM images, which indicate the formation of a superficial film providing a very good passivation on the corroded electrode in the presence of HBTC. The SEM images of carbon steel surface before corrosion (Fig. 4 (a)) and after taking place the corrosive processes in DAS (Fig. 4 (b)) and in DAS containing HBTC in different concentrations (Fig. 4 (c)-(f)) are presented.

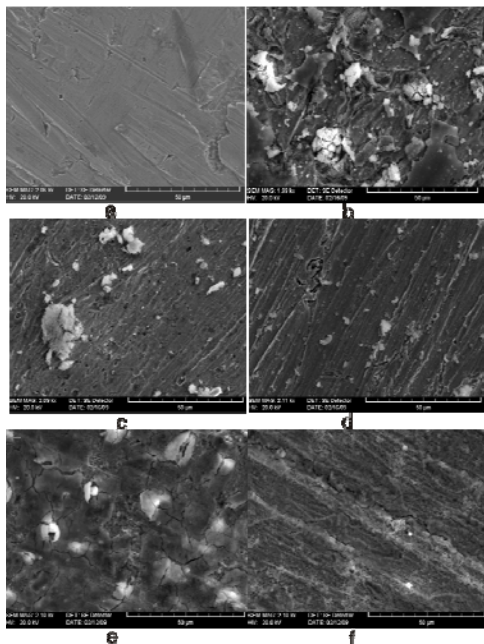


Fig. 4. SEM images of the carbon steel surface: 4a – before corrosion and after corrosion: 4b – without HBTC; 4c – DAS / 0.5 mM HBTC; 4d – DAS / 1 mM HBTC; 4e – DAS / 1.5 mM HBTC; 4f – DAS / 0.5 mM HBTC.

Fig. 4 shows the evidence of formation a thick film on the surface of carbon steel. The corrosion spots are reduced in intensity in the case of carbon steel corroded in DAS containing HBTC (Fig. 4 (c)-(f)). It can be concluded that the inhibitor molecules are adsorbed on the carbon steel surface.

3.1.5 UV-VIS spectrophotometry

Fig. 5 shows the UV-VIS spectrum of DAS without HBTC and DAS with 2 mM HBTC before and after corrosion of carbon steel in these media. The spectrum shows HBTC scanning in UV, indicating that an ionotropy of inhibitor molecular structure and the stability of this form before and after corrosion. It was observed that the absorbance of HBTC decreases after corrosion of carbon steel. This indicates that the molecules of inhibitor were adsorbed on the surface of the electrode. The presence of sulphur-atom in HBTC molecule can enhance the binding between carbon steel surface and organic compound, which consequently results in the formation of compact and impermeable self-assembled monolayer. HBTC self assembled - monolayer restrain faradaic processes such as electrode oxidation and the exchange of electrons between the electrode and solution redox couples. The property of this blocking is attributed to the compactly packed structure of the layer, which obstructs the approach of solution Cl ions to the electrode surface.

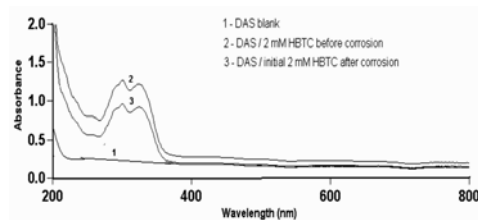


Fig. 5. UV-VIS spectrum of DAS and DAS / 2mM HBTC: 1 – DAS blank; 2 – Before corrosion of carbon steel in DAS / 2 mM HBTC; 3 – After corrosion of carbon steel in DAS / 2 mM HBTC.

4. Conclusions

HBTC is an inhibitor of carbon steel in diluted acidic media; it has an efficiency of 80.5 % obtained from tafel polarization and 82.3% from polarization resistance method, respectively. The adsorption of HBTC on the electrode surface is found to obey Langmuir's adsorption isotherm. The microscopic images of the surface of the electrode show a decrease of the corrosion spots with the increase of the HBTC concentration. This indicates a good adsorbability of HBTC on the carbon steel surface.

UV-VIS spectrophotometry confirms the adsorption process of organic compound from aqueous phase on the electrode surface.

The presence of sulphur-atom in HBTC molecule can enhance the binding between carbon steel surface and organic compound, which consequently results in the formation of compact and impermeable self-assembled layer.

Acknowledgements

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