J Solid State Electrochem (2009) 13:1297–1301
DOI 10.1007/s10008-008-0673-5

ORIGINAL PAPER

Corrosion inhibition of mild steel in hydrochloric acid by betanin as a green inhibitor

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Received: 4 December 2007 / Revised: 1 September 2008 / Accepted: 5 September 2008 / Published online: 30 September 2008

Abstract The effect of betanin (2,6-pyridinedicarboxylic acid, 4-(2-(2-carboxy-5-(beta-D-glucopyr-anosyloxy)-2,3-dihydro-6-hydroxy-1H-indol-1-yl)ethenyl)-2,3-dihydro-(*S*-(*R**,*R**))) on the corrosion inhibition of mild steel has been investigated in 1 M HCl solution. Weight loss method, potentiodynamic polarization, and electrochemical impedance spectroscopy techniques were applied to study the mild steel corrosion behavior in the absence and presence of different concentrations of betanin under the influence of various experimental conditions. The results obtained showed that betanin is a good "green" inhibitor for mild steel in 1 M HCl solution. Scanning electron microscopy observations of the steel surface confirmed the protective role of the inhibitor. The polarization curves showed that betanin behaves mainly as a mixed-type inhibitor. Maximum inhibition efficiency (98%) is obtained at betanin concentrations of 0.01 M. The results obtained from weight loss, polarization, and impedance measurements are in good agreement.

Keywords Corrosion inhibition · Betanin · Steel · Adsorption

Introduction

Acid solutions are commonly used in the chemical industry to remove the scales from metallic surfaces. The addition of inhibitors secures the metal against an acid attack effectively. The applicability of organic compounds as corrosion inhibitors for metals in acidic media has been recognized for a long time [1–3]. The existing data show that most organic inhibitors act by adsorption on the metal surface. These compounds are adsorbed on the metallic surface blocking the active corrosion sites. Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and the environment that should be replaced with new environmentally friendly corrosion inhibitors. From the viewpoint of safety, the development of non-toxic and effective inhibitors is considered to be more important and desirable. Recently, these compounds have been developed; they range from rare earth elements [4, 5] to plant extracts [6, 7]. Raja and Sethuraman [8] in a review have given natural products as a corrosion inhibitor for metals in corrosive media. The inhibition effects of some non-toxic organic compounds have been reported for steel corrosion [9, 10]. We have recently reported the inhibition effect of amino acids on steel [11], aluminum [12] corrosion and *Prunus cerasus* extract [13] on mild steel in acidic media. Betanin is a natural product and food additive. This compound is a red glycosidic pigment obtained from beetroot [14]. Betanin is a water-soluble compound that is a desirable characteristic for an acid inhibitor. However, its effect on corrosion processes of metals and alloys has not been reported.

The aim of this work is to investigate the inhibiting influence of betanin as a green inhibitor on mild steel corrosion in 1 M hydrochloric acid solution. Weight loss method, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques were used in this study. The surface of mild steel samples in 1 M HCl solution with and without the inhibitor was studied by scanning

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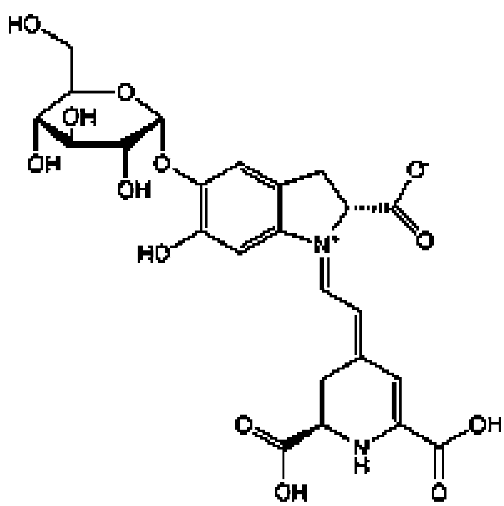
electron microscopy (SEM) to evaluate the inhibitor effect on surface morphology.

Experimental

Prior to all measurements, the mild steel specimens (0.027% P; 2.08% Si; 0.034% Cr; 0.014% W; 0.018% Mo; 0.260% Mn; 0.008% C; 0.005% S; 0.016% Ni; 0.353% Al and the remainder Fe) were ground with different emery papers (grade 400, 600, 800, 1000, and 1200), rinsed with double distilled water, degreased in absolute ethanol, and dried by compressed air at room temperature. The aggressive solutions were made of AR grade 37% HCl. Appropriate concentrations of acid were prepared using double distilled water. The concentration range of the inhibitor employed was 6.25×10^{-4} to 0.01 M in acid solutions. Required betanin with high purity was purchased from the Corporation of ABCR. Figure 1 shows the structure of betanin. All experiments were performed under the atmospheric ambient, and the temperature of the solutions was controlled by thermostat (Memert).

Weight loss experiments were performed according to the method described previously [11]. Tests were conducted in 1 M HCl solution with different concentrations of inhibitor. At the end of each test, the specimen was carefully washed in absolute ethanol, dried and then was reweighed. Duplicate experiments were performed in each case and the mean value of the weight loss was reported. Electrochemical experiments were carried out using an Autolab (PGSTAT 30). A three-electrode arrangement was used for electrochemical studies. Working electrode was prepared from a mild steel sheet, mounted in polyester so that the area exposed to the corrosive solution was 1 cm^2. A saturated calomel electrode (SCE) and a 1 cm × 1 cm platinum electrode were used as the reference and counter electrodes, respectively. For potentiodynamic polarization measurements, the potential sweep rate was 1 mV s^{-1}. The immersion time before each measurement was 60 min to access an equilibrium potential. The impedance measurements were carried out in the frequency range of 30 kHz to 0.01 Hz at the open circuit potential, by applying 10 mV sine wave ac voltage. The morphology of the surface of mild steel in 1 M HCl solution in the absence and presence of 0.01 M of betanin was investigated by SEM images obtained by a leo-440i electron microscope.



$C_{24}H_{26}N_2O_{13}$

Fig. 1 Chemical structure and formula of betanin

Table 1 Weight loss data of mild steel in 1 M HCl for various concentrations of betanin

Inhibitor concentration (M)	W_{corr} (mg/cm^2 h)	η_w
Blank	5.72	–
6.25×10^{-4}	1.77	69
1.25×10^{-3}	0.971	83
2.50×10^{-3}	0.554	90
5.00×10^{-3}	0.212	96
1.00×10^{-2}	0.129	98

Results and discussion

Weight loss studies

The weight loss of the mild steel in 1 M HCl with and without various concentrations of betanin is determined

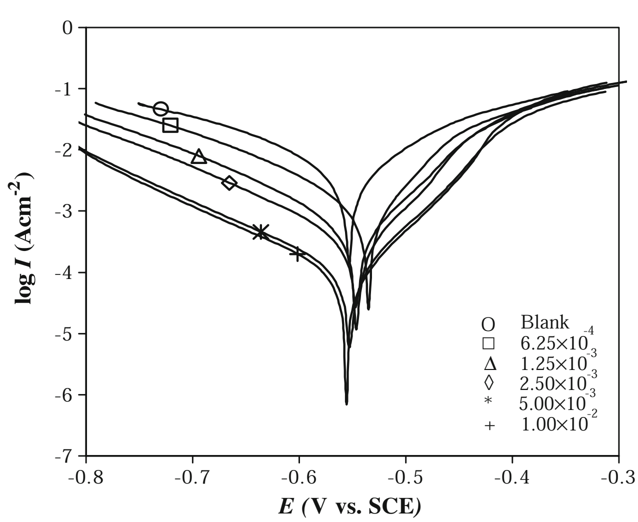


Fig. 2 Potentiodynamic polarization curves for mild steel in 1 M HCl containing different concentrations of betanin

Table 2 Potentiodynamic polarizations parameters of mild steel in 1 M HCl for various concentrations of betanin

Inhibitor concentration (M)	E_{corr} (mV vs. SCE)	β_a (mV/dec)	β_c (mV/dec)	I_{corr} (A/cm^2)	r_{corr} (mm/y)	η_p
Blank	−554	121	51	3.29×10^{-3}	38.2	–
6.25×10^{-4}	−535	98	52	7.54×10^{-4}	8.64	77.4
1.25×10^{-3}	−546	95	61	3.92×10^{-4}	4.54	88.1
2.50×10^{-3}	−546	101	55	2.60×10^{-4}	3.01	92.1
5.00×10^{-3}	−552	101	62	1.01×10^{-4}	1.17	96.9
1.00×10^{-2}	−555	105	60	7.72×10^{-5}	0.89	97.6

Table 3 Electrochemical impedance measurement of mild steel in 1 M HCl for various concentrations of betanin

Inhibitor concentration (M)	R_s (Ω cm^2)	R_t (Ω cm^2)	CPE (μF)	η_z
Blank	1.4	7.5	304	–
6.25×10^{-4}	1.2	22	130	66
1.25×10^{-3}	1.1	45	56	83
2.50×10^{-3}	1.1	78	46	90
5.00×10^{-3}	1.1	188	17	96
1.00×10^{-2}	0.9	229	10	97

after 6 h of immersion at 25 °C. Equation 1 determines the inhibition efficiency, where W_{corr} and W_0 are the corrosion rates of mild steel with and without the inhibitor, respectively. Values of the inhibition efficiency obtained are given in Table 1.

$$\eta_w = \frac{W_0 - W_{corr}}{W_0} \times 100 \tag{1}$$

The inhibition efficiency η_w increases with increasing inhibitor concentration to reach 98% at 0.01 M. The inhibition may be due to adsorption of betanin on the mild steel surface.

Potentiodynamic polarization curves

Figure 2 shows the influence of betanin concentration on the cathodic and anodic potentiodynamic polarization curves of steel in 1 M HCl. Electrochemical corrosion parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slops (β_c, β_a), and corrosion current density (I_{corr}), obtained by extrapolation of Tafel lines, are collected in Table 2. Equation 2 was used to calculate the inhibition efficiency (η_p) where I_0 and I_{corr} are the corrosion current density values without and with the inhibitor, respectively.

$$\eta_p = \frac{I_0 - I_{corr}}{I_0} \times 100 \tag{2}$$

Figure 2 and Table 2 show that the I_{corr} values decrease considerably with the increase of betanin concentration. No definite trend was observed in the shift of E_{corr} values, in the presence of various concentrations of this inhibitor, in acidic media. The presence of the inhibitor lowers the cathodic Tafel slope values probably by blocking the metal surface. The change of the anodic Tafel slope clearly indicated the influence of betanin on the mechanism of the corrosion process [15]. For potentials higher than −420 mV vs. SCE, the presence of betanin did not change the current vs. the potential. This potential can be defined as the desorption potential. The same results have been reported with other organic compounds [16, 17]. This fact means that the inhibition mode of betanin depends on the electrode potential. However, betanin influences the anodic reactions at potentials more negative than −420 mV vs. SCE. This result indicates that betanin exhibits both cathodic and anodic inhibition effects. This suggests a mixed-type control. Betanin mainly acts as a mixed-type inhibitor in 1 M HCl.

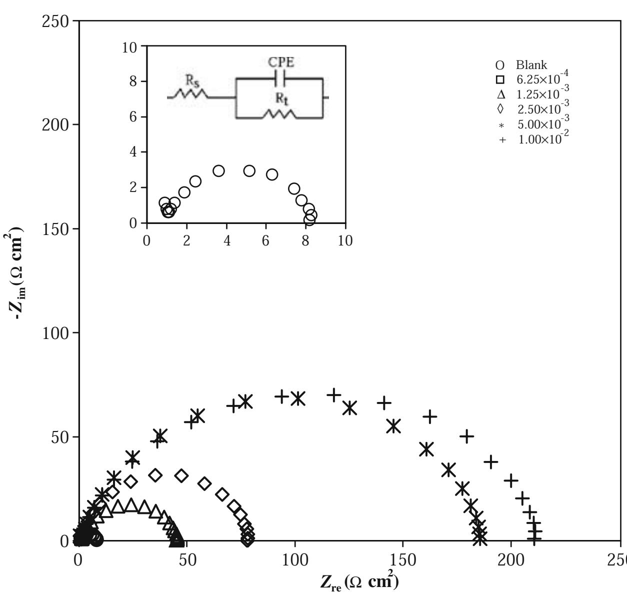


Fig. 3 Nyquist diagrams for mild steel in 1 M HCl containing different concentrations of betanin

Table 4 Effect of temperature on the inhibition efficiency of betanin in 1 M HCl with (I_{corr}) and without (I_0) of 0.01 M of inhibitor

T (°C)	I_0 (A/cm^2)	I_{corr} (A/cm^2)	η_p
25	3.29×10^{-3}	7.72×10^{-5}	97.6
35	6.59×10^{-3}	1.97×10^{-4}	97.0
45	1.24×10^{-2}	5.12×10^{-4}	95.8
55	1.32×10^{-2}	5.94×10^{-4}	95.5

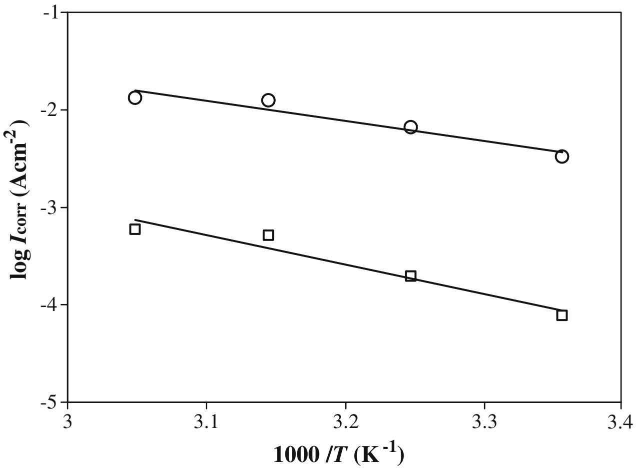


Fig. 4 Arrhenius slopes calculated from corrosion current density for mild steel in 1 M HCl: (*empty circle*) blank and (*empty square*) 0.01 M of betanin

Electrochemical impedance measurements

The corrosion behavior of mild steel in acidic solution in the presence of betanin was investigated by the EIS at 25 °C. Nyquist plots are shown in Fig. 3. The impedance response of mild steel is significantly changed after the addition of betanin. The charge transfer resistance (R_t) and the interfacial double layer capacitance (CPE) values were derived by using the equivalent circuit shown in Fig. 3. The equivalent circuit elements calculated by the Zview fitting program are given in Table 3. The inhibition efficiency (η_z) is calculated from the following equation:

$$\eta_z = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \times 100 \quad (3)$$

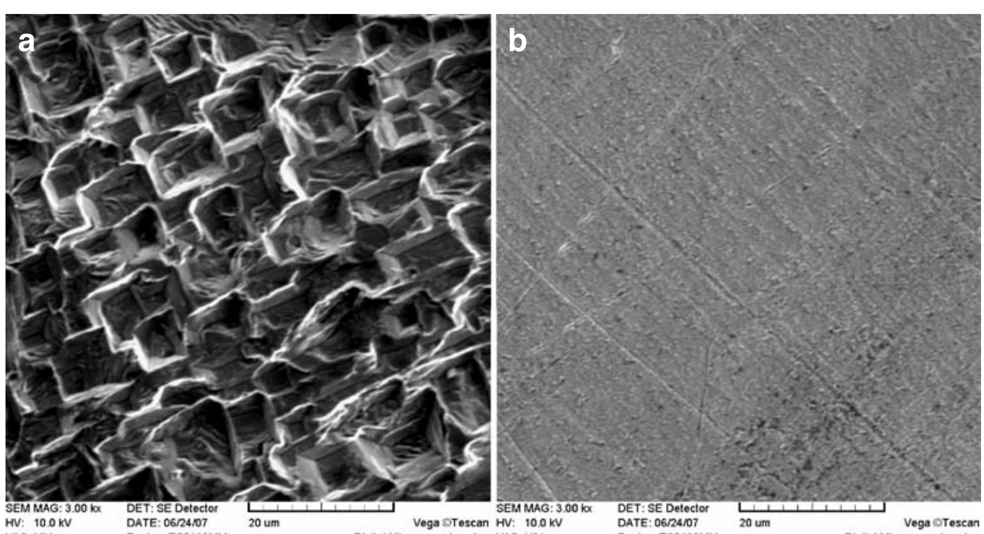
where $R_{t(inh)}$ and R_t are the charge transfer resistance values with and without the inhibitor, respectively. The R_t values were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru et al. [18].

The inhibition efficiencies, calculated from impedance results, show the same trend as those obtained from polarization and weight loss measurements. There is good agreement between the weight loss measurements and electrochemical methods. In fact, the presence of betanin is accompanied by the increase of the value of R_t in an acidic solution indicating a charge-transfer process mainly controlling the corrosion of steel. The decrease of CPE is due to the adsorption of the inhibitor on the metal surface [19].

Effect of temperature

Temperature can modify the interaction between the steel electrode and the acidic media without and with the betanin inhibitor. The values of inhibition efficiency obtained from polarization curves (are not show) for mild steel in 1 M HCl in the absence and presence of betanin at the temperature range 25–55 °C are given in Table 4. These results indicate that the corrosion current density increases more rapidly with temperature in the absence of the inhibitor. In the presence of betanin, surface coverage θ, defined by $\eta_p/100$, decreases slightly with increasing temperature, which could be caused by desorption of the inhibitor from the steel surface. The slight decrease of θ suggests that the inhibition efficiency of betanin is independent of temperature. Therefore, betanin acts as an efficient inhibitor in the range of temperature studied.

Fig. 5 SEM photograph (×3,000) of the surface for mild steel after 6 h of immersion in 1 M HCl: **a** without and **b** with 0.01 M of betanin



The apparent activation energy for the corrosion process is calculated from Arrhenius type plot according to the following equation [20]:

$$I_{corr} = A \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where E_a is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius pre-exponential constant, and T is the absolute temperature. Arrhenius plots for the corrosion current density of mild steel are given in Fig. 4. The obtained values for E_a in 1 M HCl with the absence and presence of betanin are 39.4 and 57.9 kJ/mol, respectively. It can be found that the energy barrier of corrosion reaction increases with the inhibitor concentration. This phenomenon may be attributed to the change in the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules. It is often interpreted by physical adsorption leading to the formation of an adsorptive film of electrostatic character [21, 22]. Under acidic conditions, betanin degrades to several compounds having the chemical structures that behave as inhibitors [23]. The inhibition of betanin or its degradation products in 1 M HCl was attributed to adsorption through electrostatic interactions between the negatively charged metal surface and the positively charged compounds [24]. When mild steel was immersed in the HCl solution, in the presence of inhibitor, chloride ions are firstly adsorbed to the metal surface because of a smaller degree of hydration. Adsorbed chloride ions create an excess negative charge towards the solution and favor more adsorption of the cations [25]. Positively charged inhibitor compounds or protonated inhibitor molecules are adsorbed on the metal surface via Cl^- ions which forms interconnecting bridges between the metal atoms and the organic cations.

Figure 5 shows a SEM photograph recorded for mild steel samples exposed for 6 h in 1 M HCl solution without (a) and with (b) betanin (0.01 M) at 25 °C. The morphology of the specimen surface in Fig. 5a reveals that in the absence of betanin the surface is highly corroded. However, in presence of the inhibitor, the rate of corrosion is suppressed, as the electrode surface is almost free from corrosion due to the adsorption of the inhibitor on the mild steel surface.

Conclusions

From the overall experimental results and discussion, the following conclusions can be deduced:

- The inhibition efficiency of betanin increases with concentration to attain a maximum value of 98% at 0.01 M of betanin.
- Betanin acts as mixed-type inhibitor modifying the hydrogen reduction mechanism.
- The results obtained from weight loss, potentiodynamic polarization, and EIS techniques were in good agreement.
- The inhibition of corrosion of mild steel in 1 M HCl by betanin may be due to the adsorption of betanin on the mild steel surface.

Acknowledgment The authors thank the Research Office of the University of Tabriz for finacial support.

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