

## Study of *Stevia rebaudiana* Leaves as Green Corrosion Inhibitor for Mild Steel in Sulphuric Acid by Electrochemical Techniques

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The inhibition for the corrosion of mild steel in sulphuric acid solution by the extract of *Stevia rebaudiana* leaves has been studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the leaves extract. The effect of temperature on the corrosion behavior of mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with addition of extract was also studied. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. The adsorption of the extract on the mild steel surface obeys the Langmuir adsorption isotherm. The activation energy as well as other thermodynamic parameters ( $E_a$ ,  $\Delta H$  and  $\Delta S$ ) for the inhibition process was calculated. These thermodynamic parameters show strong interaction between inhibitor and mild steel surface. The results obtained show that the extract of *Stevia rebaudiana* leaves could serve as an effective inhibitor for the corrosion of mild steel in sulphuric media.

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**Keywords:** *Stevia rebaudiana*, Corrosion, Green inhibitor, Acidic solutions

### 1. INTRODUCTION

Acid solutions are widely used in industry, such as acid picking, industrial acid cleaning, acid descaling and oil-well cleaning [1]. As the most effective and economic method, inhibitors are applied in these processes to control the metal dissolution. Most of the well known acid inhibitors are organic compounds [2-4]. However, most of them are highly toxic to both human being and environment. The toxic effects of these inhibitors have led to the use of naturally occurring products as corrosion inhibitors [5].

Natural compounds containing sulphur, oxygen and nitrogen atoms are more effective as corrosion inhibitors in acid media [6]. The efficiency of these compounds mainly depends on their abilities to be adsorbed on the metal surface with the polar groups acting as the reactive centers. In recent years, there is a considerable amount of effort devoted to develop biodegradable and efficient green corrosion inhibitors which extracted from natural plants. The extracts of *Azadirachta indica*, *Fenugreek* leaves, *Zenthoxylum alatum*, *Opuntia*, *Nypa fruticans*, *Ocimum viridis*, *Phyllanthus amarus*, *Chamomile*, *Halfabar*, and *Murraya koenigii* etc. were studied as corrosion inhibitors in sulphuric and/or hydrochloric acid medium [7-13]. Recently the extract of *Medicago Sativa* has been evaluated as corrosion inhibitor which exhibited very high inhibitor efficiency on corrosion of mild steel in sulphuric acid [13].

*Stevia rebaudiana* is a species of Compositae, in which glucosides, sterols, amino acids and flavonoids are the main components. These series of compounds are rich in oxygen, nitrogen and sulphur-containing groups, which may act as green corrosion inhibitors for mild steel dissolution due to the chelating action and the formation of a physical blocking barrier on the metal surface [12]. In view of the high performance of plants extract we have investigated the inhibitive effect of *stevia rebaudiana* leaves on corrosion of mild steel in sulphuric acid with potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

## 2. EXPERIMENTAL

### 2.1 Materials

Dried *S. rebaudiana* (5g) plant leaves were soaked in  $0.5\text{molL}^{-1}$   $\text{H}_2\text{SO}_4$  (50 ml) solution for 24 h. This concentrated solution ( $0.1\text{ g ml}^{-1}$ ) was used to prepare solutions of different concentrations by dilution method. Mild steel composed of (wt%) Fe 99.30%, C 0.076%, Si 0.026%, Mn 0.192%, P 0.012%, Cr 0.050% and Ni 0.050% was used for electrochemical study. The steel specimen was embedded in Teflon holder using epoxy resin with an exposed area of  $0.29\text{ cm}^2$ . Before each experiment, the electrode was first mechanically polished with various grades of sandpaper (up to 1200 grit) and then ultrasonically cleaned in acetone for 2 min, followed by a rinse in double-distilled water.

### 2.2 Electrochemical measurements

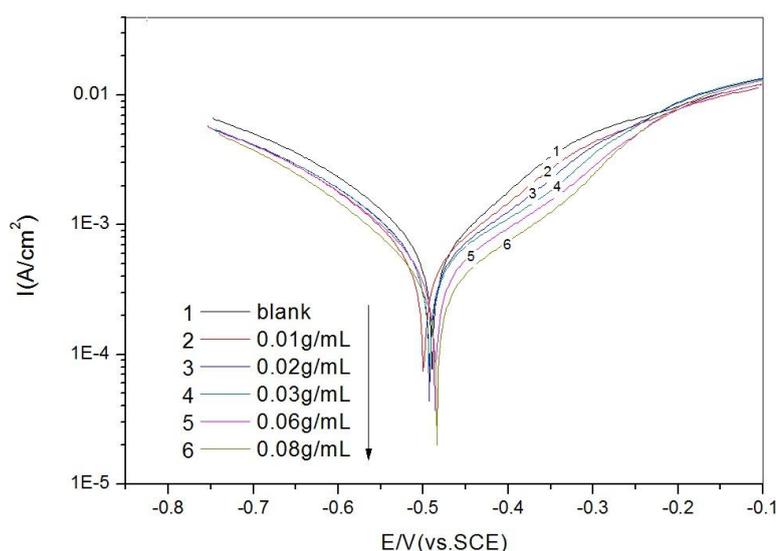
Electrochemical experiments were carried out using a CHI660B electrochemical workstation. A classical three-electrode cell, which used with a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode, was used for electrochemical measurements. Potentiodynamic polarization curves were recorded at a sweep rate of  $1\text{ mV s}^{-1}$ . Electrochemical impedance spectroscopy (EIS) measurements were carried out at open-circuit potential over a frequency range of 0.1 Hz-100 kHz. The sinusoidal perturbation was 5 mV in amplitude. Electrochemical data were obtained after 1 h of immersion with the working electrode at the rest potential, and all tests have been performed in non-de-aerated solutions under unstirred conditions. The data emulation program of the

type Stetup\_ZSimDemo\_320 was used to treat the impedance data and know the equivalent circuit which describes the reaction between solution and sample surface.

### 3. RESULTS AND DISCUSSION

#### 3.1 Potentiodynamic polarization

Polarization curves for mild steel at various concentration of *S. rebaudiana* leaves extract are shown in Fig. 1.



**Figure 1.** Polarization curves in absence and presence of different concentrations of the extract.

**Table 1.** Potentiodynamic polarization parameters for the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with different concentrations of the extract.

$C_{inh}(g\ mL^{-1})$	$E_{corr}$ (vs SCE/ V)	$i_{corr}(mA\ cm^{-2})$	$b_a$ (mV dec <sup>-1</sup> )	$b_c$ (mV dec <sup>-1</sup> )	$\eta$ (%)
Blank	-0.489	1.72	113.76	115.38	—
0.01	-0.493	1.27	128.63	120.88	25.39
0.02	-0.492	0.97	148.04	119.69	42.13
0.03	-0.491	0.53	149.05	112.13	67.52
0.06	-0.485	0.42	161.46	115.00	75.22
0.08	-0.483	0.27	181.50	108.21	90.06

The extrapolation of Tafel straight line allows the calculation of the corrosion current density ( $i_{corr}$ ). The values of  $i_{corr}$ , the corrosion potential ( $E_{corr}$ ), cathodic and anodic Tafel slopes ( $b_c$  and  $b_a$ ) and inhibition efficiency ( $\eta$ , %) are given in Table 1. The  $\eta$  (%) is defined as:

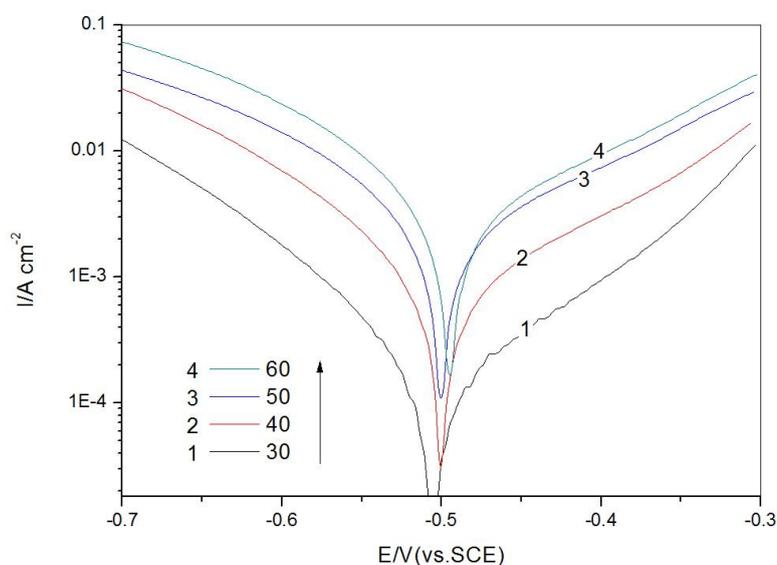
$$\eta(\%) = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100$$

where  $i_{corr}^0$  and  $i_{corr}$  are the corrosion current density values without and with inhibitor, respectively. It is very clear from Fig. 1 that both anodic and cathodic reactions of mild steel corrosion were suppressed in the presence of *S. rebaudiana* extract, and the suppression effect increases with the increasing concentration of the extract in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. No distinct change is observed in the slopes of the cathodic Tafel lines in the presence of various concentrations of extract, while the slopes of the anodic Tafel lines have an increasing trend with the increase of the concentration of extract. This result suggests that *S. rebaudiana* extract does not change the mechanism of the hydrogen evolution, whereas modify the anodic metal dissolution reaction.

As it can be seen from Table 1, corrosion current densities decrease and the inhibition efficiencies increase with the increase of extract concentrations. But it shows that there was no definite trend in the shift of  $E_{corr}$  values, which indicates that *S. rebaudiana* extract can be classified as mixed type of inhibitor in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

### 3.2 Effect of temperature

The activation parameters of corrosion process can be obtained by investigating the influence of temperature on corrosion inhibition, consequently some information about adsorption mechanism can be obtained. Polarization curves of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different temperatures (30-60°C) in presence of 0.06 g ml<sup>-1</sup> *S. rebaudiana* extract are given in Fig. 2.



**Figure 2.** Polarization curves for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.06 g ml<sup>-1</sup> *S. rebaudiana* extract at different temperature.

Electrochemical parameters are presented in Table 2. The corrosion current density increases with the increase of temperature in uninhibited and inhibited solutions.

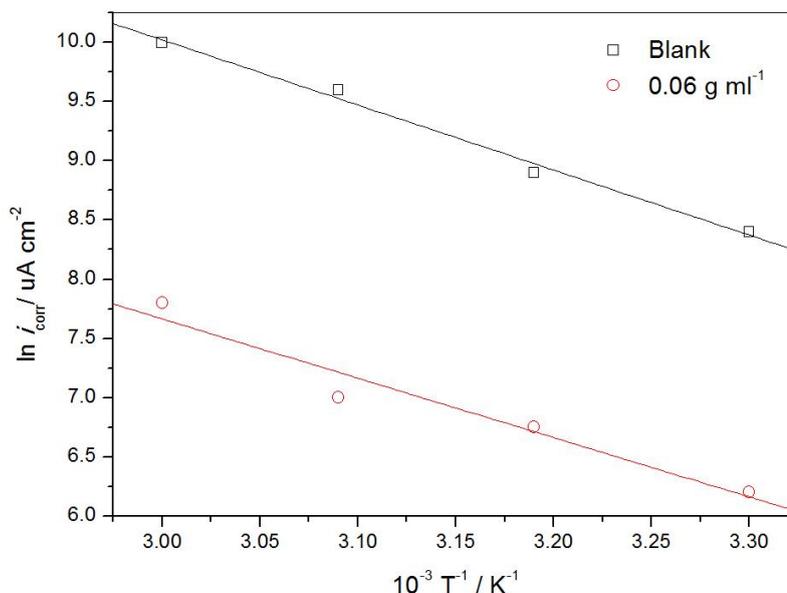
**Table 2.** Electrochemical parameters for mild steel in H<sub>2</sub>SO<sub>4</sub> without and with the extract at different temperature.

T(°C)	0.5 M H <sub>2</sub> SO <sub>4</sub>		0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.06 g mL <sup>-1</sup> extract		
	E <sub>corr</sub> (V)	i <sub>corr</sub> (×10 <sup>-3</sup> A cm <sup>-2</sup> )	E <sub>corr</sub> (V)	i <sub>corr</sub> (×10 <sup>-3</sup> A cm <sup>-2</sup> )	η (%)
30	-0.489	1.72	-0.509	0.42	75.22
40	-0.492	2.56	-0.495	0.73	71.40
50	-0.489	2.87	-0.494	0.82	69.91
60	-0.488	3.24	-0.490	0.95	60.58

In order to calculate the activation energy of the corrosion process, Arrhenius equation was used:

$$i_{corr} = k \exp\left(-\frac{E_a}{RT}\right)$$

Where *k* is the pre-exponential factor, *R* the general gas constant and *E<sub>a</sub>* is the activation energy of the corrosion process.



**Figure 3.** Arrhenius plot for ln*i<sub>corr</sub>* vs. 1/*T* in H<sub>2</sub>SO<sub>4</sub> with and without 0.06 g ml<sup>-1</sup> extract.

Fig. 3 presents the Arrhenius plot of the natural logarithm of the corrosion current density vs.  $1/T$  in the absence and presence of *S. rebaudiana* extract in 0.5 M  $H_2SO_4$ . The calculated values of activation energy are listed in Table 3.

**Table 3.** Activation parameters for the corrosion of mild steel in  $H_2SO_4$  with and without 0.06 g  $mL^{-1}$  extract.

Systems	$E_a$ (kJ $mol^{-1}$ )	$\Delta H$ (kJ $mol^{-1}$ )	$\Delta S$ (J $K^{-1} mol^{-1}$ )
0.5 M $H_2SO_4$	29.53	23.36	-119.90
0.5 M $H_2SO_4$ + 0.06 g $mL^{-1}$ extract	52.54	54.75	11.38

The inspection of Table 3 shows that the value of  $E_a$  obtained in the presence of extract is higher than that obtained in the free acid solution, which may be interpreted as physical adsorption that occurs in the first stage [3]. The increase in  $E_a$  can be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with the increase in temperature [14].

An alternative formulation of Arrhenius equation is [15]:

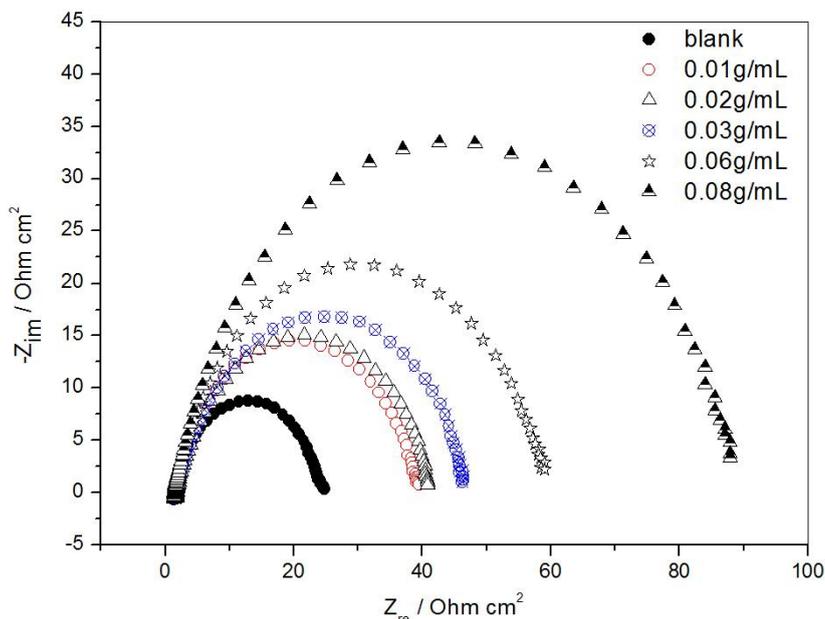
$$i_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-\Delta H}{RT}\right)$$

Where  $h$  is the plank's constant,  $N$  is Avogadro's number,  $\Delta S$  is the entropy of activation and  $\Delta H$  is the enthalpy of activation. A plot of  $\ln(i_{corr}/T)$  vs.  $1/T$  gave a straight line with the slope of  $-\Delta H/R$  and the intercept of  $\ln(R/Nh) + \Delta S/R$ , from which the values of  $\Delta S$  and  $\Delta H$  were calculated and given in Table 3. The positive signs of enthalpy ( $\Delta H$ ) reflect the endothermic nature of dissolution process. The shift towards positive value of entropy ( $\Delta S$ ) imply that the activated complex in the rate determining step represents dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex [16].

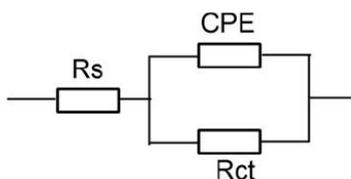
### 3.3 Electrochemical impedance spectroscopy (EIS)

The corrosion of mild steel in 0.5 M  $H_2SO_4$  in the presence of *S. rebaudiana* extract was investigated by EIS at open circuit potential. Impedance spectra for mild steel in absence and presence of different concentrations of the extract are shown in the form of Nyquist plot (Fig. 4).

These diagrams show a "depressed" semicircle with single capacitive loop, which is attributed to charge transfer of the corrosion process, and the diameters of the loops increase with the increase of the extract concentration. The impedance data were analyzed by fitting to the equivalent circuit in Fig. 5, in which  $R_s$  represents the electrolyte resistance,  $R_{ct}$  is the charge transfer resistance and CPE is a constant phase element.



**Figure 4.** Nyquist plots in absence and presence of different concentration of the extract in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 30°C.



**Figure 5.** Equivalent circuit model used to fit the impedance spectra.

Excellent fit with this model was obtained for all experimental data. The impedance of a constant phase element is described by the expression:

$$Z_{CPE} = Y_0^{-1}(j\omega)^{-n}$$

where  $Y_0$  is a proportional factor,  $n$  has the meaning of a phase shift. For  $n=0$ , CPE represents a resistance, for  $n=1$  a capacitance, for  $n=0.5$  a Warburg element and for  $n=-1$  an inductance. According to Hsu and Mansfeld [17], the value of the double-layer capacitance ( $C_{dl}$ ) can be obtained from the equation:

$$C_{dl} = Y_0(\omega'')^{n-1}$$

where  $\omega''$  is the frequency at which the imaginary part of the impedance has a maximum.

The impedance parameters such as solution resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ),  $Y_0$ ,  $n$ , double-layer capacitance ( $C_{dl}$ ) and inhibition efficiency ( $\eta$ , %) are listed in Table 3. The values of  $\eta$  are calculated by the charge transfer resistance as follows:

$$\eta(\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100$$

where  $R_{ct}$  and  $R_{ct}^0$  are the charge transfer resistance in presence and absence of inhibitor, respectively.

**Table 4.** Fitting the EIS for mild steel in  $H_2SO_4$  containing different concentration of the extract.

$C_{inh}(g mL^{-1})$	$R_s (\Omega cm^2)$	$R_{ct} (\Omega cm^2)$	$Y_0 (\mu F cm^{-2})$	$n$	$C_{dl} (\mu F cm^{-2})$	$\eta$ (%)
Blank	1.73	9.31	275.90	0.83	106.88	—
0.01	1.14	148.11	177.14	0.82	94.84	26.41
0.02	1.34	150.68	150.95	0.81	90.16	33.13
0.03	1.09	258.42	144.58	0.79	84.02	66.37
0.06	1.81	274.25	107.71	0.81	80.77	79.76
0.08	1.80	311.85	98.43	0.83	76.71	94.27

It is clear from Table 4 that by increasing the inhibitor concentration, the  $C_{dl}$  values trend to decrease and the inhibition efficiency increases. According to the Helmholtz model [18]:

$$\delta_{org} = \frac{\epsilon_0 \epsilon_r}{C_{dl}}$$

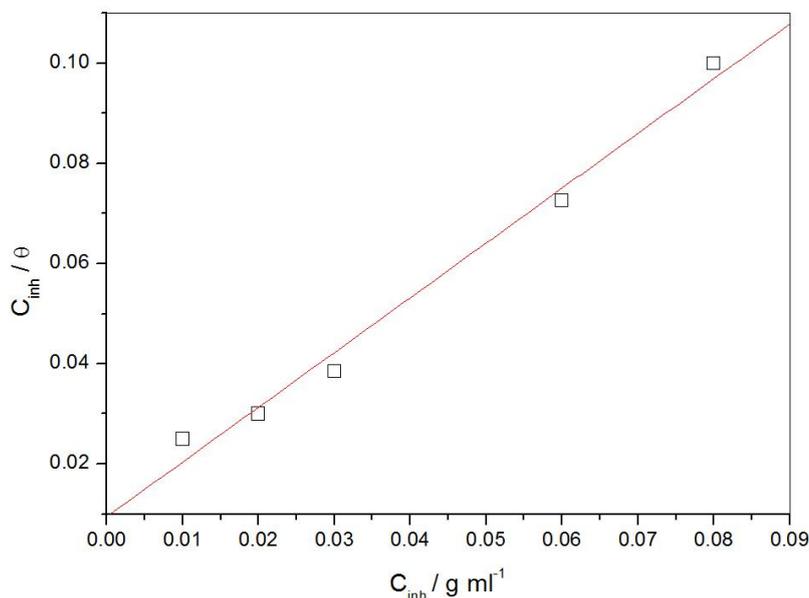
where  $\delta_{org}$  is the thickness of the protective layer,  $\epsilon_0$  is the dielectric constant and  $\epsilon_r$  is the relative dielectric constant. Therefore, the decrease in the  $C_{dl}$ , which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that *S. rebaudiana* extract functions by adsorption at the metal/solution interface as a consequence of replacement of water molecules by the extract compounds [19]. The results obtained from EIS are in good agreement with those obtained from potentiodynamic polarization methods.

### 3.4 Adsorption isotherm

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. For this purpose, the values of surface coverage ( $\theta$ ) corresponding to different concentrations of *S. rebaudiana* extract have been used to determine the adsorption isotherm. Calculation of the coverage from  $C_{dl}$  is the method used widely according to the following equation [3, 4, 8, 13]:

$$\theta = \frac{C_{dl(\theta=0)} - C_{dl,\theta}}{C_{dl(\theta=0)} - C_{dl(\theta=1)}}$$

where  $C_{dl(\theta=0)}$  and  $C_{dl(\theta=1)}$  are the double layer capacitances of the inhibitor-free and entirely inhibitor-covered surfaces, respectively.  $C_{dl,\theta}$  is the composite total double layer capacitance for any intermediate coverage  $\theta$ . Several adsorption isotherms, such as Langmuir, Temkin and Frumkin isotherms, have been tested for the description of adsorption behavior of the inhibitor. The plot of  $C_{inh}/\theta$  against  $C_{inh}$  give straight lines with the slope of 1.093, and the value of correlation coefficient is 0.983 (Fig. 6).



**Figure 6.** Langmuir adsorption isotherm plot for the adsorption of the extract in 0.5 M H<sub>2</sub>SO<sub>4</sub> on the surface of mild steel.

The results indicate that obeys the Langmuir adsorption isotherm on the mild steel surface in the sulphuric acid:

$$\theta = \frac{KC_{inh}}{1 + KC_{inh}}$$

where  $K$  is the equilibrium constant of the adsorption process. The free energy of adsorption process  $\Delta G_{ads}^0$  can be calculated from the equation [4]:

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^0}{RT}\right)$$

The value of  $\Delta G_{ads}^0$  from the Langmuir adsorption isotherm in 0.5 M H<sub>2</sub>SO<sub>4</sub> was calculated to be -29.1 kJ mol<sup>-1</sup>. Generally, values of  $\Delta G_{ads}^0$  around -20 kJ mol<sup>-1</sup> or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption); those

around  $-40 \text{ kJ mol}^{-1}$  or higher involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [20]. The calculated  $\Delta G_{ads}^0$  value shows, therefore, that the adsorption mechanism of the extract on steel involves both two types of interaction. Indeed, due to the strong adsorption of water molecules on the surface of mild steel, one may assume that adsorption occurs first due to the physical force. The removal of water molecules from the surface is accompanied by chemical interaction between the metal surface and adsorbate, and that turns to chemisorptions [2]. In sum, the large negative values of  $\Delta G_{ads}^0$  reveal that the adsorption process takes place spontaneously and the adsorbed layer on the surface of mild steel is highly stable [21]. This is in good agreement with the results obtained from impedance spectroscopy and polarization measurements.

#### 4. CONCLUSIONS

The examined extract of *S. rebaudiana* leaves inhibits the corrosion of mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  and found to be good efficiency. Polarization curves indicated that *S. rebaudiana* extract acts as mixed type inhibitor in  $\text{H}_2\text{SO}_4$  solution. The inhibition is accomplished by adsorption of the extract components on the iron surface, and the adsorption is spontaneous and obeys the Langmuir isotherm.

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