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# *Schinopsis lorentzii* Extract As a Green Corrosion Inhibitor for Low Carbon Steel in 1 M HCl Solution

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**ABSTRACT:** The corrosion inhibition of low carbon steel in 1 M HCl solution with different concentrations of *Schinopsis lorentzii* extract was studied using Tafel extrapolation, linear polarization, and electrochemical impedance spectroscopy (EIS). It was found that *Schinopsis lorentzii* extract acted as slightly cathodic inhibitor and inhibition efficiencies increased with the increase of extract concentration. The adsorption of the molecules of the extract on the low carbon steel surface was in accordance with the Temkin adsorption isotherm. The results showed that *Schinopsis lorentzii* extract could serve as a corrosion inhibitor of the low carbon steel in hydrochloric acid environment.

## 1. INTRODUCTION

Low carbon steel is most widely used as a constructional material in many industries due to its excellent mechanical properties and low cost maintenance. It is used in large tonnages in marine applications, chemical processing, petroleum production and refining processes, construction, and metal processing equipment. Acid solutions are commonly used in industry, for example, chemical cleaning, descaling, pickling, and oil-well acidizing, petrochemical processes, erecting boilers, drums, heat exchangers, tanks, etc., which leads to corrosive attack. Corrosion prevention employing inhibitors is one of the most common, effective, and economic methods to protect metals in acidic media.<sup>1–3</sup> Therefore, the consumption of inhibitors to reduce corrosion has increased in recent years.

Due to increasing ecological awareness and strict environmental regulations, as well as the inevitable drive toward sustainable and environmentally friendly processes, attention has been now focused toward the development of nontoxic alternatives to inorganic and organic inhibitors applied so far. Currently, research in corrosion is oriented to the development of “green corrosion inhibitors”, compounds with good inhibition efficiency but low risk of environmental pollution.<sup>4,5</sup> Plant extracts are biodegradable and constitute incredibly rich sources of natural chemical compounds that can be extracted by simple procedures at low cost.<sup>6</sup> Thus, since the 1990s, many investigations have been related to the evaluation of natural compounds as corrosion inhibitors. For instance, some amino acids, vitamins, and plant extracts have been tested.<sup>7–11</sup> The basic components of extracts are sugars, gallic acid, ellagic acid, and flavanoids.<sup>12</sup> Even the presence of tannins, cellulose, and polycyclic compounds normally enhances the film formation over the metal surface, thus decreasing corrosion.<sup>13</sup>

*Schinopsis lorentzii* (Quebracho Colorado Santiagueño) is a hardwood tree, native of the Paraguayan subtropical area, which forms forests in Gran Chaco region of Argentina, in Paraguay, and in Bolivia. *Schinopsis lorentzii*, belongs to the Anacardiaceae family and is a vigorous tree that reaches up to 25 m in height and 1.5 m in diameter.<sup>14,15</sup> They have been widely applied in bridge construction, flooring (industrial heavy traffic), joinery, ladders,

light construction, marine construction, mine timbers, railroad ties, sporting goods, turnery, and vehicle parts.<sup>16</sup> *Schinopsis lorentzii* wood has extraordinary resistance against decay. However, not much attention has been paid to this extract as a source of corrosion inhibition.

The present work was established to study the corrosion inhibition of low carbon steel in 1 M HCl solution by employing novel plant extract *Schinopsis lorentzii* derivatives as a potential corrosion inhibitor using different techniques including potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS). The thermodynamic parameters were also calculated and discussed.

## 2. EXPERIMENTAL APPROACH

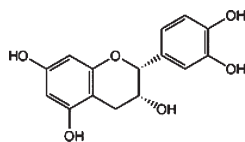
**2.1. Materials.** Electrochemical measurements were carried out in a three-electrode type cell with separate compartments for the reference electrode (Ag/AgCl), and the counter electrode was platinum (Pt) plate. The working electrode was low carbon steel. Low carbon steel (AISI 1026) had the composition (wt %) 0.22–0.28 C, 0.90–1.10 Mn, 0.3 Ni, 0.3 Cr, 0.04 (max) P, 0.05 (max) S, and the rest Fe. The area of this electrode was 0.5 cm<sup>2</sup>, and the surface of the working electrode was prepared by grinding abrasive paper of 400–1800 gradation. Next, they were rinsed with distilled water and degreased with acetone. Before each measurement, the sample was immersed in a corrosion cell and allowed to stabilize for 30 min.<sup>17,18</sup> *Schinopsis lorentzii* extracts were easily dissolved at room temperature with double distilled water. Mixtures of 100, 500, 1000, and 2000 ppm of *Schinopsis lorentzii* extract were prepared using 37% HCl obtained from Merck. Corrosion behavior of low carbon steel in 1 M HCl environment with different concentrations of *Schinopsis lorentzii* extract was investigated. *Schinopsis lorentzii* extracts were obtained from Indunor S.A., Buenos Aires, Argentina. It is the powder

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**Figure 1.** The main flavonoid monomer (flavan-3-ol) for *Schinopsis lorentzii* extract.

version of the solid *Schinopsis lorentzii* tree, which is obtained by water extraction. In addition, the extraction procedure was conducted according to ASTM 1110-96 and TAPPI T204 OM-88 standard.<sup>19</sup> CHNS content (wt %) was calculated using a CHNS analyzer (Loco, USA). This analysis showed the presence of carbon (44.60%), hydrogen (5.02%), nitrogen (0.29%), sulfur (0.02%), and oxygen (rest).

**2.2. Stiasny Test.** The Stiasny test, a widely used method, served as a simple, fast, and reproducible estimation of condensed tannin contents.<sup>20</sup> The Stiasny number of the extracts, a measure of the formaldehyde condensable polyphenol content, was determined according to the procedure proposed by Yazaki and Hillis.<sup>21</sup> *Schinopsis lorentzii* extract was first dried under vacuum for at least 24 h to give an accurate weight. After the dry sample was dissolved in 10 mL of water, 1 mL of 10 M HCl and 2 mL of formaldehyde (37%) were added, and the mixture was heated under reflux for 30 min. The reaction mixture was filtered while hot through a sintered glass filter. The precipitate was washed with hot water ( $5 \times 10$  mL) and dried over  $\text{CaCl}_2$ .<sup>22</sup> The yield of tannin was expressed as a percentage of the weight of the starting material. Condensed tannin content of *Schinopsis lorentzii* extract is (wt %) 88.32.<sup>23</sup> Condensed tannins are oligomers constituted by flavonoid repeating units as shown in Figure 1. Flavan-3-ol has been reported as main flavonoid monomer for *Schinopsis lorentzii* extract.<sup>24,25</sup>

**2.3. Method.** **2.3.1. Potentiodynamic Polarization Measurements.** Potentiodynamic polarization curves and linear polarization resistance (LPR) measurements were performed using a Gamry Instrument potentiostat/galvanostat/ZRA. Polarization curves were recorded at a constant sweep rate of 1 mV/s at a  $-400$  to  $+400$  mV interval with respect to open circuit potential ( $E_{\text{corr}}$ ). Corrosion current density values,  $I_{\text{corr}}$ , were calculated by using the Tafel extrapolation method and by taking an extrapolation interval of  $\pm 250$  mV around the  $E_{\text{corr}}$  value once stable.<sup>26</sup> The polarization resistance ( $R_p$ ) from Tafel extrapolation method was calculated using the Stern–Geary equation (eq 1),<sup>27</sup> where  $\beta_a$  and  $\beta_c$  were anodic and cathodic Tafel slopes respectively.

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p} \quad (1)$$

LPR measurements were carried out by polarizing the specimen from  $+25$  to  $-25$  mV with respect to  $E_{\text{corr}}$  at a scanning rate of  $0.125 \text{ mV/s}^{-1}$ . The  $R_p$  values were calculated according to eq 2.

$$I_{\text{corr}} = \frac{B}{R_p} \quad (2)$$

where  $B$  is the proportionality constant, which equals  $0.026 \text{ V}$  for a particular system.<sup>28</sup>

**2.3.2. Electrochemical Impedance Spectroscopy (EIS).** Electrochemical impedance spectroscopy (EIS) was performed using a Gamry Instrument potentiostat/galvanostat/ZRA. Electrochemical

impedance spectroscopy measurements were carried out at open  $E_{\text{corr}}$  by using an amplitude signal of  $10 \text{ mV}$  in a frequency range of  $50 \text{ mHz}$  to  $100 \text{ kHz}$ .

### 3. RESULTS AND DISCUSSION

**3.1. Potentiodynamic Polarization Measurements.** Figure 1 shows the anodic and cathodic polarization curves of low carbon steel in  $1 \text{ M HCl}$  solution, without and with  $100$ ,  $500$ ,  $1000$ , and  $2000 \text{ ppm}$  of *Schinopsis lorentzii* extract. It was observed that both the cathodic and anodic curves showed lower current density in the presence of the *Schinopsis lorentzii* extract derivatives than those recorded in the solution without *Schinopsis lorentzii* extract derivatives. This indicates that *Schinopsis lorentzii* extract inhibits the corrosion process. The results in Figure 2 also suggested that the studied extract affects both anodic and cathodic corrosion processes; hence it reveals properties of a mixed type inhibitor. But there are also changes in corrosion potential ( $E_{\text{corr}}$ ). The addition of plant extracts changes the values of  $E_{\text{corr}}$  to the cathodic direction, So *Schinopsis lorentzii* extract can be considered as a slightly cathodic inhibitor. The electrochemical parameters, that is, corrosion current density ( $I_{\text{corr}}$ ), anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) Tafel constants, and polarization resistance ( $R_p$ ), are shown in Table 1.

It can be observed that the concentration of inhibitor has a little influence on values of anodic Tafel constant ( $\beta_a$ ) and more significant influence on the values of cathodic Tafel constant ( $\beta_c$ ) indicating that inhibitor may change the mechanism of cathodic reaction and may not affect the process of anodic dissolution.<sup>29</sup>

The data in Table 1 clearly show that the current density ( $I_{\text{corr}}$ ) values decreased and the polarization resistance ( $R_p$ ) values increased in the presence of various concentrations of *Schinopsis lorentzii* extracts as expected. Due to the inverse relationship between  $I_{\text{corr}}$  and  $R_p$ , with increasing concentration of the inhibitor, it can be assumed that the adsorption of the inhibitor molecules on metal surface makes a physical barrier for the mass and charge transfer, providing a high degree of protection to the metal surface.

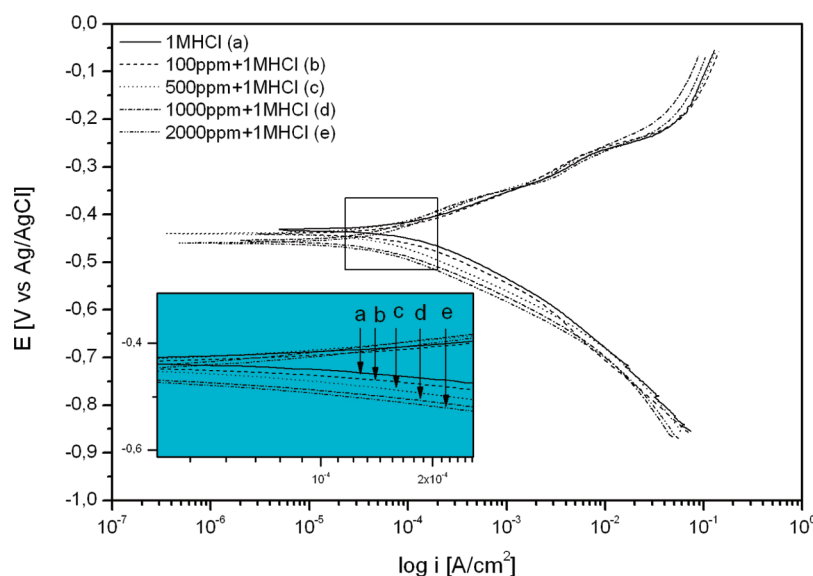
The LPR and TP results were found to be similar (Table 2). The inhibition efficiency (IE%) was computed for low carbon steel in  $1 \text{ M HCl}$  solutions containing  $100$ ,  $500$ ,  $1000$ , and  $2000 \text{ ppm}$  of *Schinopsis lorentzii* extract from the Tafel plots and polarization resistance measurements are shown in Table 3. The IE% values were obtained from  $I_{\text{corr}}$  and  $R_p$  data using eqs 3 and 4.

$$\text{IE}(\%) = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100 \quad (3)$$

$$\text{IE}(\%) = \left( 1 - \frac{R_p^0}{R_p} \right) \times 100 \quad (4)$$

where  $I_{\text{corr}}$  and  $R_p^0$  are the corrosion current density and the polarization resistance, respectively, measured in solutions without inhibitor and  $I_{\text{corr(inh)}}$  and  $R_p$  are the same parameters determined in solutions containing inhibitor.

The IE% values obtained from the TP experiments ( $I_{\text{corr}}$ ) were higher than those obtained through the LPR ( $R_p$ ). This behavior suggests that the inhibitor action is dependent on the potential applied and time of polarization, since in the  $R_p$  experiments only  $\pm 25 \text{ mV}$  around  $E_{\text{corr}}$  was applied to the working electrode and the duration of the experiment was shorter.<sup>30</sup> However, the data



**Figure 2.** Potentiodynamic polarization curves for low carbon steel in 1 M HCl at various concentration of the inhibitor (a) blank, (b) 100 ppm, (c) 500 ppm, (d) 1000 ppm, (e) 2000 ppm.

**Table 1.** Electrochemical Parameters Obtained from Potentiodynamic Polarization Plots of Low Carbon Steel Immersed in 1 M HCl Medium and Different Concentration of the Inhibitor

| inhibitor concentration (ppm) | $\beta_a$ (mV dec <sup>-1</sup> ) | $\beta_c$ (mV dec <sup>-1</sup> ) | $I_{corr}$ ( $\mu$ A cm <sup>-2</sup> ) | $E_{corr}$ (mV) | $R_p$ ( $\Omega$ cm <sup>2</sup> ) |
|-------------------------------|-----------------------------------|-----------------------------------|---|-----------------|------------------------------------|
| 0                             | 84.5                              | 108.5                             | 116                                     | -432            | 178                                |
| 100                           | 81.4                              | 104.2                             | 95.1                                    | -439            | 209                                |
| 500                           | 78.3                              | 95.4                              | 51.7                                    | -441            | 361                                |
| 1000                          | 73.4                              | 86.1                              | 45.5                                    | -455            | 386                                |
| 2000                          | 62.8                              | 88.6                              | 38.3                                    | -460            | 417                                |

**Table 2.** Electrochemical Parameters Obtained from LPR Results for Low Carbon Steel Immersed in 1 M HCl and for Different Concentration of the Inhibitor

| inhibitor concentration (ppm) | $E_{corr}$ (mV) | $I_{corr}$ ( $\mu$ A cm <sup>-2</sup> ) | $R_p$ ( $\Omega$ cm <sup>2</sup> ) |
|-------------------------------|-----------------|---|------------------------------------|
| 0                             | -439            | 132                                     | 197                                |
| 100                           | -447            | 110                                     | 237                                |
| 500                           | -453            | 70                                      | 372                                |
| 1000                          | -459            | 58                                      | 449                                |
| 2000                          | -463            | 49                                      | 532                                |

clearly showed that the low carbon steel electrochemical corrosion rate decreased in the presence of *Schinopsis lorentzii* extract.

**3.2. Electrochemical Impedance Spectroscopy (EIS).** The corrosion behavior of low carbon steel in 1 M HCl solution in the presence of *Schinopsis lorentzii* extract was investigated by EIS at room temperature after 30 min of immersion. Figure 3 shows the results of EIS experiments in the Nyquist representation. The general shape of the curves is very similar for all samples; the shape is maintained throughout the whole concentration range, indicating that almost no change in the corrosion mechanism occurred due to inhibitor addition.<sup>31,32</sup> From these Nyquist plots, the values of the charge-transfer resistance ( $R_{ct}$ ) were

**Table 3.** Percentage Inhibition Efficiency (IE%) of *Schinopsis lorentzii* Extract as an Inhibitor of Low Carbon Steel Corrosion in 1 M HCl Computed Based on TP and LPR Techniques

| inhibitor concentration (ppm) | TP IE% | LPR IE% |
|-------------------------------|--------|---------|
| 0                             |        |         |
| 100                           | 18     | 17      |
| 500                           | 55     | 47      |
| 1000                          | 60     | 56      |
| 2000                          | 66     | 63      |

obtained from the difference in the real component ( $Z_{re}$ ) of impedance at lower frequencies.<sup>33</sup> It is evident from Nyquist plots that they are significantly changed on addition of inhibitors (Figure 3).

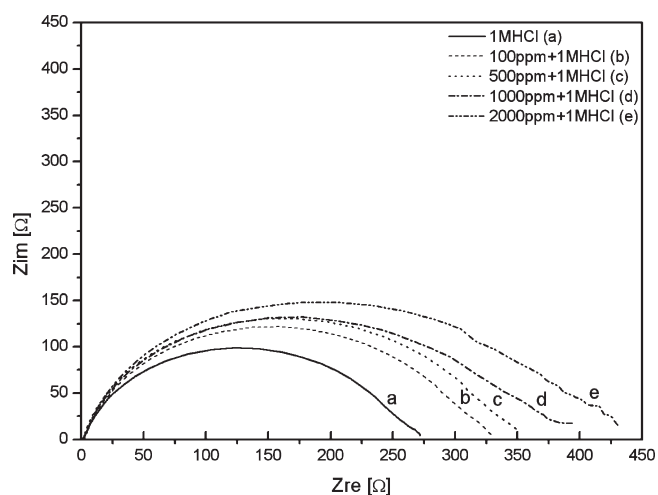
The Nyquist plots are analyzed with ZSimpwin 3.10 program.<sup>34</sup> This program provides good information about circuit. In order to acquire more quantitative information about the adsorption mechanism, electrical analysis of the experimental data was performed. An equivalent electrical circuit that fitted the best impedance data was introduced in Figure 4. As a result, the following electrical parameters were determined (Table 4): the charge transfer resistance ( $R_{ct}$ ), surface heterogeneity ( $n$ ), and constant phase element ( $Q$ ).

Table 4 demonstrates that the increase in the  $R_{ct}$  values leads to an increase of inhibition efficiency. The results indicate good agreement between the values of corrosion efficiency as obtained from the impedance technique and polarization measurements. It is concluded that the corrosion rate depends on the chemical nature of the electrolyte rather than the applied technique.<sup>35</sup>

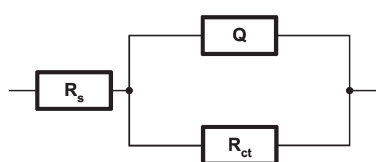
Parameter  $Q$  describes the nonideal behavior of capacitance. The impedance of constant phase element (CPE) is given by eq 5.

$$Z(\text{CPE}) = [Q(j\omega)^n]^{-1} \quad (5)$$

where  $j$  is the imaginary number,  $Q$  is the frequency independent real constant,  $\omega = 2\pi f$  is the angular frequency (rad/s),  $f$  is the frequency of the applied signal, and  $n$  is the CPE exponent for



**Figure 3.** Nyquist plots for low carbon steel in 1 M HCl in the absence and presence of different concentrations of *Schinopsis lorentzii* extract.



**Figure 4.** An electrical circuit of R(QR) model. Key:  $R_s$ , resistance of electrolyte in bulk;  $R_{ct}$ , charge transfer resistance at the metal surface;  $Q$ , constant phase element.

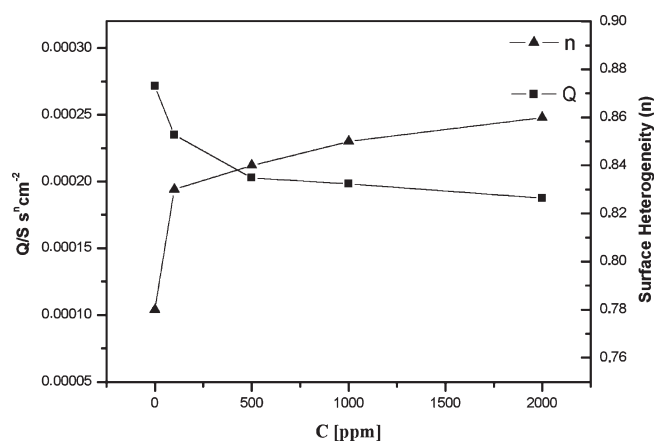
**Table 4.** EIS Data for Low Carbon Steel in 1 M HCl in the Absence and Presence of Different Concentrations of *Schinopsis lorentzii* Extract

| inhibitor concentration<br>(ppm) | $R_{ct}$ ( $\Omega \text{ cm}^2$ ) | $Q$ ( $Q/S, \text{s}^n \text{ cm}^{-2}$ ) | $n$  | IE%   |
|----------------------------------|------------------------------------|---|------|-------|
| 0                                | 127                                | 0.0002716                                 | 0.78 |       |
| 100                              | 158                                | 0.0002349                                 | 0.83 | 19.60 |
| 500                              | 167                                | 0.0002026                                 | 0.84 | 24.00 |
| 1000                             | 186                                | 0.0001983                                 | 0.85 | 31.70 |
| 2000                             | 207                                | 0.0001877                                 | 0.86 | 38.60 |

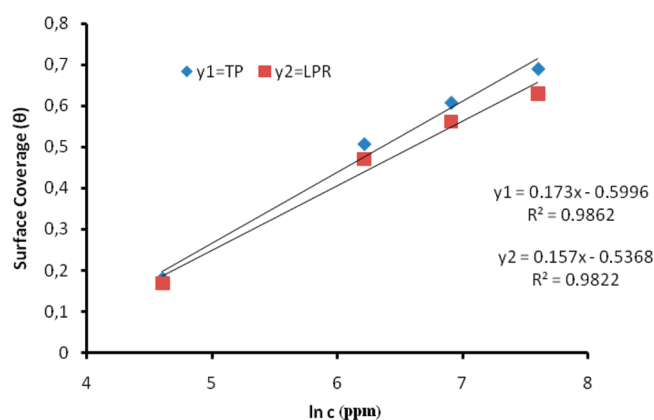
whole number of  $n = 1, 0, -1$ . CPE is reduced to the classical lump element capacitor (C), resistance (R), and inductance (L). The value of  $n$  equal to 0.5 corresponds to Warburg impedance (W). The dispersion of the capacitive semicircle can be related to surface heterogeneity due to surface roughness or inhibitor adsorption and formation of porous layer.<sup>36,37</sup>

In this sense,  $n$  serves as a measure of surface heterogeneity. Figure 5 shows the values of  $n$  and  $Q$  vs concentration of *Schinopsis lorentzii* extracts in 1 M HCl solution. The low values of  $Q$  correspond with high values of the  $n$  parameter as can be seen from Figure 5. In addition, low values of the  $Q$  parameter indicate that water molecules were possibly replaced by inhibitor molecules. Thus it proves that a layer of the inhibitor was formed at the metal/solution interface improving corrosion inhibition.<sup>30</sup>

The increase in inhibitor concentration increases the charge transfer resistance ( $R_{ct}$ ) and surface coverage ( $\theta$ ) values that are calculated from eq 7. In this case, the heterogeneity factor ( $n$ ) value approaches one. There are also too many papers in literature



**Figure 5.** Surface heterogeneity ( $n$ ) and CPE ( $Q$ ) values vs concentration ( $C$ ) of *Schinopsis lorentzii* extract in 1 M HCl solution.



**Figure 6.** Surface coverage ( $\theta$ ) as a function of logarithm of inhibitor concentration determined from TP (◆) and LPR (■) measurements.

**Table 5.** Thermodynamic Parameters Acquired from Temkin Adsorption Isotherm in Case of Both Tafel and Linear Polarization Techniques

| alloy | Tafel polarization |   | linear polarization |   |
|-------|--------------------|---|---------------------|---|
|       | $K_{ads}$ (lt/mg)  | $-\Delta G^\circ$ (kJ mol <sup>-1</sup> ) | $K_{ads}$ (lt/mg)   | $-\Delta G^\circ$ (kJ mol <sup>-1</sup> ) |
| ST3   | 0.0312             | 1.36                                      | 0.0327              | 1.48                                      |

**Table 6.** FT-IR Transmittance Spectra of *Schinopsis lorentzii* Extract and Their Identification

| peaks from FT-IR spectra, $\nu$ (cm <sup>-1</sup> ) | possible groups                    |
|---|------------------------------------|
| 650.8–975.7   | $\equiv \text{C}-\text{H}$ bending |
| 1037.3  | OH stretch                         |
| 1284.9  | O–SO <sub>2</sub> –O               |
| 1371.7  | C–N stretch                        |
| 1450.2  | X–SO <sub>2</sub> –X/–C–N–H– bend  |
| 1519.4  | aromatic C=C stretching            |
| 1614.7  | C=N stretch                        |
| 3367.5  | O–H stretch or N–H stretch         |

about this statement.<sup>38–40</sup> The meaning of heterogeneity factor ( $n$ ) has been discussed in eq 5. The increase in charge



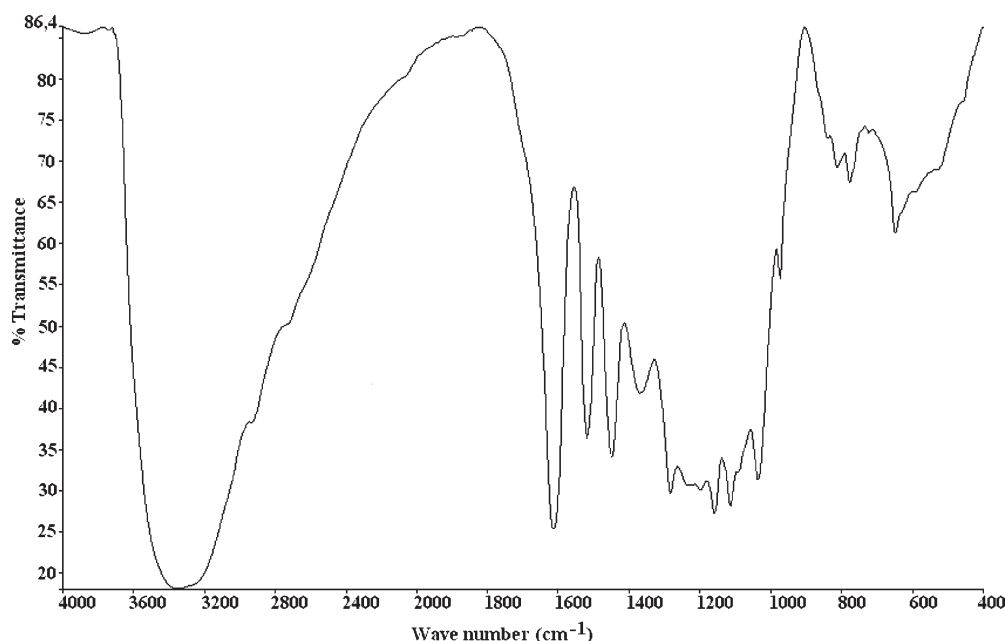


Figure 7. FT-IR transmittance spectra of *Schinopsis lorentzii* extract (inhibitor).

transfer resistance with inhibitor concentration suggests that more inhibitor molecules are adsorbed on the metal surface at higher concentration leading to greater surface coverage. This can be attributed to the decrease in surface heterogeneity, thus, improvement in corrosion inhibition.<sup>41</sup>

The values of  $n$ , ranging between 0.78 and 0.86, indicate that the charge transfer process controls the dissolution mechanism of the low carbon steel in 1 M HCl solution in the absence and in the presence of the extract.

The percentage inhibition efficiency (IE%) was calculated from the charge transfer resistance ( $R_{ct}$ ) values by using eq 6.

$$IE(\%) = \frac{R_{ct}^{-1} - R_{ct(inh)}^{-1}}{R_{ct}^{-1}} \times 100 \quad (6)$$

where the  $R_{ct(inh)}$  and  $R_{ct}$  are the charge transfer resistance values with and without inhibitor. Calculated IE% values are shown in Table 4.

**3.3. Adsorption Isotherms.** It is generally assumed that the adsorption of inhibitor on the metal surfaces is the essential step in the mechanism of inhibition. The establishment of isotherms that describe the adsorption behavior of corrosion inhibitors is essential because they provide important clues about the nature of metal inhibitor interaction. The degree of surface coverage ( $\theta$ ) for different concentrations of inhibitor was evaluated from LPR and TP measurements. The experimental data were tested graphically by fitting to various isotherms. Adsorption isotherm for *Schinopsis lorentzii* extract on the surface of the low carbon steel in 1 M HCl is shown in Figure 6. A straight line was obtained on plotting  $\theta$  against  $\ln c$ , suggesting that the adsorption of the compound on the low carbon steel surface follows the Temkin adsorption isotherm model.<sup>42</sup> From the straight lines in the  $\theta$  vs  $\ln c$  graph, equilibrium constants for the adsorption process,  $K_{ads}$ , are obtained.<sup>43</sup>

Determination of the type of adsorption isotherm takes into account that the degree of surface coverage,  $\theta$ , as a function of inhibitor concentration  $c$ . The surface coverage ( $\theta$ ) values were

calculated from eq 7.

$$\theta = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \quad \text{or} \quad \theta = \left(1 - \frac{R_p}{R_p^*}\right) \quad (7)$$

According to the equation describing the Temkin adsorption model (eq 8), the  $\theta$  element depends on the equilibrium adsorption constant ( $K$ ), the molecular interaction constant ( $f$ ), and concentration ( $c$ ).<sup>44</sup>

$$e^{f\theta} = K_{ads}c \quad (8)$$

In addition, knowledge of the  $K$  parameter allows calculation of the free energy adsorption ( $\Delta G^\circ$ ) based on eq 9.

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G^\circ}{RT}\right) \quad (9)$$

where 55.5 is the concentration of water in the solution in mol dm<sup>-3</sup>,  $K$  = equilibrium adsorption constant,  $R$  = the universal gas constant, and  $T$  = the thermodynamic temperature.

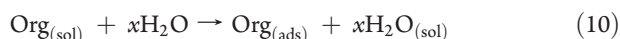
As can be seen from Figure 6, the plot has higher linear correlation coefficients when TP data are used. Thermodynamic parameters for the adsorption of *Schinopsis lorentzii* extract on the low carbon steel calculated from Temkin adsorption isotherms using surface coverage ( $\theta$ ), calculated from the results of both TP and LPR, are indicated in Table 5. The values of free energy of adsorption ( $\Delta G_{ads}^\circ$ ) that were obtained from eq 9 are negative, which reveals the spontaneity of the adsorption process and the stability of the adsorbed layer on the low carbon steel.<sup>45</sup> It is generally accepted that with the values of  $\Delta G_{ads}^\circ$  up to  $-20$  kJ mol<sup>-1</sup>, the types of adsorption were regarded as physisorption and the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal. In contrast for the values around  $-40$  kJ mol<sup>-1</sup> or smaller, interactions were seen as chemisorptions, which is due to the charge sharing or a

charge transfer from the inhibitor molecules to the metal surface to form covalent bond.<sup>46,47</sup>

The  $\Delta G_{\text{ads}}^{\circ}$  values obtained in this study range from  $-1.36$  to  $-1.48 \text{ kJ mol}^{-1}$ . It suggested that the adsorption mechanism of the *Schinopsis lorentzii* extract derivatives on low carbon steel in 1 M HCl solution was typical of physisorption. Similar low values of  $\Delta G_{\text{ads}}^{\circ}$  also obtained by several researchers.<sup>48,49</sup>

**3.4. Inhibition Mechanism.** The observed corrosion inhibition of low carbon steel in 1 M HCl solution with increase in *Schinopsis lorentzii* extract concentration can be explained by the adsorption of the components of the *Schinopsis lorentzii* extract on the metal surface. The main tannin molecule in *Schinopsis lorentzii* extract is flavan-3-ol (Figure 1). This molecule contains oxygen atoms in functional groups (O–H, C=C, C–H, C–O) and an aromatic ring, which meets the general consideration of typical corrosion inhibitors. In acidic media, the nonbonded electrons of oxygen get protonated. Due to electrostatic interaction, the protonated constituent's molecules are adsorbed (physisorption), and inhibition is expected.<sup>50</sup>

The corrosion rate of low carbon steel in 1 M HCl solution is controlled by both a hydrogen evolution reaction and a dissolution reaction of this metal. It is generally accepted that the corrosion inhibition occurs due to adsorption of organic molecules at the metal/solution interface, and the adsorption itself depends on the molecule's chemical composition, the temperature and the electrochemical potential at the metal/solution interface. In fact, the solvent  $\text{H}_2\text{O}$  molecules could also adsorb at the metal/solution interface.<sup>51</sup> Therefore, the adsorption of organic inhibitor molecules from aqueous solution can be regarded as a substitution adsorption process between the organic compound in the aqueous phase [ $\text{Org}_{(\text{sol})}$ ] and water molecules on the metal surface [ $\text{H}_2\text{O}_{(\text{ads})}$ ].<sup>52</sup>



where  $x$  is the size ratio, that is, the number of water molecules replaced by one organic inhibitor. According to the detailed mechanism above, displacement of some adsorbed water molecules might take place on the metal surface by inhibitor species. The increase in efficiency of inhibition of *Schinopsis lorentzii* extract indicates that the inhibitor molecules are adsorbed on the low carbon steel surface with higher concentration, leading to greater surface coverage ( $\theta$ ). It is generally has been proven that the first step in the adsorption of an organic inhibitor on a metal surface usually involves the replacement of one or more of water molecules adsorbed at the metal surface by the investigated extract molecules.<sup>53</sup>

**3.5. FT-IR Spectral Studies.** A transmission vibrational spectrum of *Schinopsis lorentzii* extract is depicted in Figure 6 and the FT-IR peaks are given in Table 6. In Figure 7, the broad peak at  $3367.5 \text{ cm}^{-1}$  indicates the presence of hydroxyl group overlapped by the strong stretching mode of N–H.<sup>54,55</sup> The appearance of the peak in the region of  $1614.7 \text{ cm}^{-1}$  corresponds to the C=N symmetric stretching vibration of this group. The peak at  $1519.2 \text{ cm}^{-1}$  is attributed to the stretching mode of the aromatic ring (C=C).<sup>56</sup> The presence of a C–N stretching frequency is clearly manifested in the region of  $1371.7 \text{ cm}^{-1}$ . A series of peaks identified between  $650.8$  and  $975.7 \text{ cm}^{-1}$  correspond to the very strong  $\equiv\text{C}-\text{H}$  bending of terminal alkynes and very strong asymmetric aliphatic P–O–C stretch/aromatic and heteroaromatic C–H stretch. The peaks at  $1284.9$  and  $1450.2 \text{ cm}^{-1}$  are attributed to the functional group O–SO<sub>2</sub>–O occurrence of very

strong secondary alkyl sulfate salts and X–SO<sub>2</sub>–X of sulfuryl halides and C–N–H bend.<sup>29</sup> The peak at  $1037.3 \text{ cm}^{-1}$  is attributed to the –OH group.<sup>56</sup> This shows that this plant extract contains mixtures of compounds, that is, alkaloids, flavonoids, and oils.<sup>57</sup>

## 4. CONCLUSIONS

- 1 Polarization measurements demonstrate that *Schinopsis lorentzii* extract acts as slightly cathodic inhibitor for corrosion of low carbon steel in 1 M HCl medium and the inhibition efficiency of low carbon steel in 1 M HCl medium increases with increasing the concentration of *Schinopsis lorentzii* extract.
- 2 The electrochemical methods used in this study (TP, LPR, EIS) show similar results considering the inhibition efficiency of *Schinopsis lorentzii* extract. The differences between applied methods depend on measurement techniques. However, all methods clearly demonstrate that *Schinopsis lorentzii* extract shows inhibition properties on low carbon steel in 1 M HCl medium.
- 3 *Schinopsis lorentzii* extract is a natural and environmentally benign product it can be used as an alternative for toxic chemical inhibitors in acidization and acid pickling of mild steel.
- 4 Stiasny test analysis of *Schinopsis lorentzii* extract shows that this plant extract contains 88.32 wt % condensed tannin. As parallel to the previous studies on tannins, this research reveals that tannins can be used as an inhibitor in acidic media for low carbon steel.
- 5 The values of free energy ( $\Delta G^{\circ}$ ) of adsorption of inhibitor molecules on the low carbon steel surface suggest that the inhibition behavior of *Schinopsis lorentzii* extract involve as physisorption and is found to obey the Temkin adsorption isotherm.

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